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FUNDAMENTAL STUDIES FOR DEVELOPMENT OF ELECTROCHEMICAL COD AND --ETC(U)

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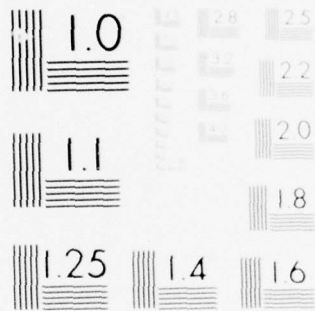
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FUNDAMENTAL STUDIES FOR DEVELOPMENT OF ELECTROCHEMICAL COD AND TOC ANALYZERS (U)

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ANNUAL REPORT

by

R. J. Davenport and R. A. Wynveen

September 1977

Project Officer: William J. Cooper
Environmental Protection Research Division
US Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, MD 21701



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Life Systems, Inc.
Cleveland, Ohio 44122

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The essential components of the Electrochemical COD and TOC Analyzers have been assembled, tested and evaluated. In situ electrochemical generation of per-sulfate has been demonstrated. Sensors to monitor persulfate and carbon dioxide in the analyzers have been developed and tested. The sensors have demonstrated the ability to measure chemical oxygen demand (COD) and total organic carbon (TOC) concentrations. Therefore, compact, portable, simple and relatively low cost analyzers may be developed using these components for use in field (cont.)		

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19. continued

Medical Unit, Self-Contained, Transportable
Electrode
Platinum
Rotating Disk Electrode
Total Organic Carbon
Chemical Oxygen Demand
Persulfate
Oxidation
Sensors
Carbon Dioxide
Breadboard
Coulometric Sensor
Potentiometric Sensor
Membrane Electrode
In Situ Generation

20. continued

Applications. An advantage is that in situ generation of persulfate in the analyzers will allow them to operate without consumables. Also, a single analyzer that can measure both COD and TOC concentrations is a demonstrated possibility. Results, conclusions and recommendations are presented.

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Prepared Under Contract DAMD17-76-C-6077

by

LIFE SYSTEMS, INC.
Cleveland, Ohio 44122

for

U. S. Army Medical Bioengineering
Research and Development Laboratory
Ft. Detrick, MD 21701

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EXECUTIVE SUMMARY

Electrochemical Chemical Oxygen Demand and Total Organic Carbon Analyzers were conceptually designed for a feasibility evaluation under Contract DAMD17-75-C-5070. The analyzer design goals included the capability for simple, automated monitoring of organic solute concentrations throughout the range of 0.5 to 30 ppm chemical oxygen demand and 0.1 to 10 ppm total organic carbon. They were designed for on-line field applications, and the designs therefore include the features of continuous operation and in situ generation of the required reagent. Electrochemical generation of reagents avoids the necessity of supplying reagents to the analyzers in the field, and minimizes their logistic demands. Because of the simplicity of the analyzer designs, the end-item analyzers are anticipated to be lower cost than commercially available, process-oriented analyzers.

The evaluation of the analyzer conceptual designs indicated that three components were essential to the operation of the analyzers. Prior to further development of the analyzers, experimental testing and evaluation of those components were required to determine their performance limitations and to identify any special requirements of the components needed for successful integration in the analyzers.

The objective of this program was to develop and test for evaluation breadboard versions of the essential analyzer components. The electrochemical cell used for generation of persulfate, the reagent used in the analyzers, is one of the components. Sensors for monitoring persulfate and carbon dioxide are the other components tested during the program. The persulfate sensor is used for determining chemical oxygen demand concentrations, while a membrane type of carbon dioxide electrode is used for measurement of total organic carbon values.

The tests of the components demonstrated that they meet the requirements for use in the Electrochemical Chemical Oxygen Demand and Total Organic Carbon Analyzers. The persulfate generation cell operated well and has almost twice the maximum capacity required by the analyzers. The persulfate and carbon dioxide sensors exhibited detection limits sufficient to permit detection of 0.5 ppm chemical oxygen demand and 0.1 ppm total organic carbon. They are capable of measuring at least 140 ppm chemical oxygen demand and 500 ppm total organic carbon, respectively, with the operating conditions anticipated for use in the analyzers.

The repeatability of the components, and the small effects of potential inorganic and organic interferences on the performance of the persulfate generation cell and sensors, indicate that they are capable of providing accurate and precise chemical oxygen demand and total organic carbon data when they are later integrated in an analyzer. To attain the utmost accuracy, automated daily calibration is recommended as a feature of the end-item analyzer.

The tests performed during this program have also demonstrated that integration of the persulfate and carbon dioxide sensors in a single analyzer to permit monitoring both chemical oxygen demand and total organic carbon values may be possible. Therefore, the end-item of this development may be an Electrochemical Total Organic Carbon Analyzer, an Electrochemical Chemical Oxygen Demand

Analyzer, or an Electrochemical Total Organic Carbon/Chemical Oxygen Demand Analyzer.

The common factor in all three analyzers is the oxidation of organic solutes by persulfate. The accuracy of total organic carbon and chemical oxygen demand values obtained with the analyzers may be limited by the quantitative efficiency of this oxidation process. Therefore, it is recommended that total organic carbon and chemical oxygen demand data be obtained with a breadboard version of the Electrochemical Total Organic Carbon/Chemical Oxygen Demand Analyzer. This data will be compared to that collected using standard methods, and the analytical performance that can be expected from an end-item analyzer will be evaluated. Based on the results of this evaluation, later development of a completely automated, on-line analyzer may be possible.

FOREWORD

The analytical and experimental work described herein was performed by Life Systems, Inc. under U.S. Army Contract DAMD17-76-C-6077 during the period September 1, 1976 to August 31, 1977. The program was directed by Dr. R. J. Davenport. The technical effort was completed by Dr. R. J. Davenport, J. D. Powell, T. S. Steenson and Dr. R. A. Wynveen.

Mr. William J. Cooper was the Contract Project Officer representing the U.S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, MD 21701. Mr. Larry Lobring was the Project Officer representing the Environmental Monitoring and Support Laboratory, Environmental Protection Agency, Cincinnati, OH, 45268. Dr. Deh Bin Chan and Mr. Richard Saam represented the Civil Engineering Laboratory at Port Hueneme, CA, 93010. Maj Emil Frein and Cpt Gary McNutt represented the Water and Solid Resources Division at Tyndall Air Force Base, FL, 32401.

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ACRONYMS

COD	Chemical Oxygen Demand
IRAD	Internal Research and Development
MTBF	Mean-Time-Between-Failures
MUST	Medical Unit, Self-Contained, Transportable
RDE	Rotating Disk Electrode
SCE	Saturated Calomel Electrode
TOC	Total Organic Carbon
TSA	Test Support Accessories
UV	Ultraviolet
WPE	Water Processing Element

INTRODUCTION

There is a need for simple, low-cost and on-line chemical oxygen demand (COD) and total organic carbon (TOC) analyzers for field applications. Increasing concern about the purity of water and control of organic pollutants will result in greater use of such analyzers in water treatment laboratories and process control applications.

Some applications require the use of COD or TOC analyzers in remote areas. The Water Processing Element (WPE) of the Medical Unit, Self-Contained, Transportable (MUST) Army Field Hospital is an application of that type. The analyzers used in the WPE or in other remote sites should operate without consumption of reagents or compressed gases to minimize logistic demands. Also, since the analyzers will be transported in the field, either individually or as part of a larger system, the analyzer should be compact, lightweight and portable. For the analyzer to be widely accepted, it must be low cost, reliable and simple to operate.

During contract DAMD17-75-C-5070, the conceptual designs of the Electrochemical COD and TOC (1) Analyzers were developed, and a feasibility analysis of them was performed. The analyzers were designed to have the characteristics necessary for use in the field, and the initial application considered was the MUST WPE.

Both analyzers are based on the principle of oxidation of organic solutes in water samples using persulfate ($S_2O_8^{2-}$), with sensors to measure either carbon dioxide (CO_2) produced by the oxidation of the organics, or the concentration of persulfate consumed during the oxidation. The CO_2 evolved is proportional to the TOC concentration in the sample, and the concentration of persulfate consumed in the oxidation is proportional to the COD content. The analyzer designs include the feature of in situ, electrochemical generation of the persulfate in an electrolyte recycle loop that avoids the requirement of supplying the analyzers with reagents. The simple design of the analyzers is compatible with automated operation, small size and weight, portability and relatively low cost.

An additional feature of the analyzers is that costly and polluting reagents are not required. The standard COD method and automated variations of it result in the discharge into the environment of significant quantities of dichromate ($Cr_2O_7^{2-}$), silver (Ag^+) and mercury (Hg^{2+}) salts. The Electrochemical COD and TOC Analyzers do not use $Cr_2O_7^{2-}$, Ag^+ or Hg^{2+} and retain the persulfate within the electrolyte recycle loop. If any persulfate is discharged, it will rapidly decompose to form sulfate (SO_4^{2-}) which is not a pollutant.

The evaluation of the analyzer designs revealed that many similarities exist between the Electrochemical COD and the Electrochemical TOC Analyzers. It may therefore be possible to combine the persulfate and pCO_2 sensors into a single analyzer capable of monitoring both COD and TOC values, or the ratio of COD to

(1) References cited in parentheses are listed at the end of this report.

TOC. The ratio of COD to TOC may be valuable in some applications for distinguishing the type of organic solutes in the water samples. For instance, humic acids may be distinguished from industrial pollutants by the COD to TOC ratios.

Because of the flexibility in combining sensors in the analyzers to result in either a TOC, a COD, or a TOC/COD analyzer, this development may result in more than one analyzer. Each analyzer may be used in specific applications. For applications in which industrial wastes are monitored, a COD analyzer may be useful. In other applications where water is processed for reuse or for consumption, TOC may be the required water quality index. Therefore, the present analyzer development is anticipated to result in a number of analyzers that can be tailored to specific applications.

The objective of this program was to test and evaluate the performance of the essential analyzer components identified during Contract DAMD17-75-C-5070. The components were tested under conditions projected to be those used in future Electrochemical COD and TOC Analyzers. The components were evaluated to insure that the analytical performance of the analyzers will not be limited by the components initially selected during the feasibility analysis.

The persulfate generation cell and the persulfate and pCO_2 sensors were tested and evaluated, and they have been shown to satisfactorily provide the quality of performance necessary for the analyzers. It is concluded that an Electrochemical TOC/COD Analyzer, containing the components, can now be assembled for analytical testing and comparison to standard methods.

Definitions

Both COD and TOC are commonly used indices of organic solute concentrations and are defined below:

1. Chemical Oxygen Demand: COD represents the oxygen (O_2) equivalents consumed in the chemical oxidation of oxidizable solutes (primarily organic species). The COD in the sample is determined by measuring the quantity of a strong chemical oxidizing agent consumed during oxidation of the solutes. COD is expressed as mg/l.
2. Total Organic Carbon: TOC values represent the concentration of carbonaceous organic solutes in the sample, expressed in terms of milligrams of carbon per liter of sample.

Analyzer Conceptual Designs

The conceptual designs developed during contract DAMD17-75-C-5070 are described below.

Electrochemical COD Analyzer

The conceptual design of the Electrochemical COD Analyzer is shown in Figure 1. To avoid consumption of reagents, an electrolyte recycle loop is part of the design. The water sample is continuously injected into the electrolyte re-

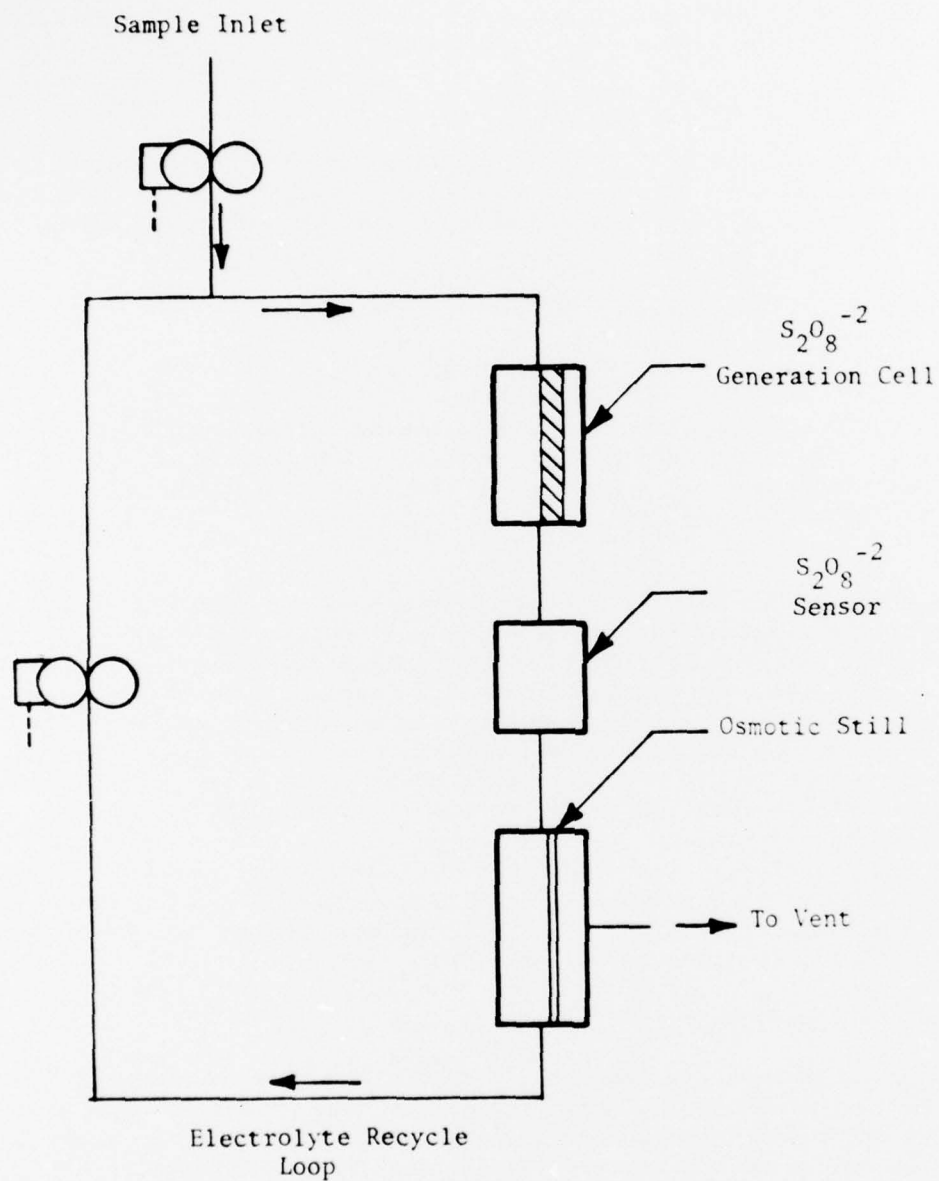


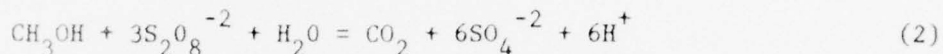
FIGURE 1 ELECTROCHEMICAL COD ANALYZER SCHEMATIC

cycle loop with a flow rate that equals that of the electrolyte. Persulfate is generated in situ in the electrochemical cell shown in the schematic by oxidation of SO_4^{-2} in the electrolyte (Equation 1).



The oxidation of organic solutes by the persulfate occurs in the area between the persulfate generation cell and the persulfate sensor. The reaction is often catalyzed by ultraviolet (UV) radiation. The UV radiation zone is not shown in the schematics for simplification.

A typical oxidation is shown for methanol in Equation 2.



During the oxidation, persulfate is consumed and the organic solutes are oxidized to CO_2 . The persulfate sensor monitors the concentration of the persulfate remaining after the organics are completely oxidized, and the decrease in the persulfate concentration is proportional to the COD content of the sample.

The water injected at the sample inlet must be eliminated from the electrolyte recycle loop or the electrolyte concentration will change. The osmotic still, which is basically a vacuum distillation device that uses porous membrane to contain the electrolyte, can eliminate from 6 N sulfuric acid (H_2SO_4) as much as 0.0028 cc/min of water per cm^2 of membrane area. This is accomplished by heating the still to 93C and controlling the pressure on the vapor side of the still to values between 2 and 6 psia. Under these conditions, only 80 to 90 cm^2 of membrane area is required to remove the water from the recycle loop when the sample and electrolyte flow rates are each 0.1 ml/min. The osmotic still has been documented in the literature⁽²⁾. Therefore, the capability of removing water from the electrolyte recycle loop exists. However, later work may indicate that simpler, smaller, and more reliable devices exist for performing the water elimination function in the analyzers.

Electrochemical TOC Analyzer

The TOC content of the water sample can be determined by measuring the CO_2 produced by the oxidation of the organic solutes. The oxidation of the organics may be carried out with electrochemically generated persulfate, as shown in Equation 2. The output of a CO_2 sensor in the analyzer downstream of the oxidation zone is proportional to the organic carbon concentration (Figure 2). As in the Electrochemical COD Analyzer, an electrolyte recycle loop is incorporated into the Electrochemical TOC Analyzer concept to minimize the quantity of electrolyte that must be contained in the analyzer and supplied to it.

A second CO_2 sensor upstream of the persulfate generation cell is included in the conceptual design to determine the inorganic carbon concentration in the sample. The CO_2 sensor downstream of the persulfate generation cell measures the sum of the CO_2 from the inorganic and organic carbon after oxidation of the organics by persulfate. The sensor control circuitry electronically determines the TOC concentration from the difference in the response of the two sensors.

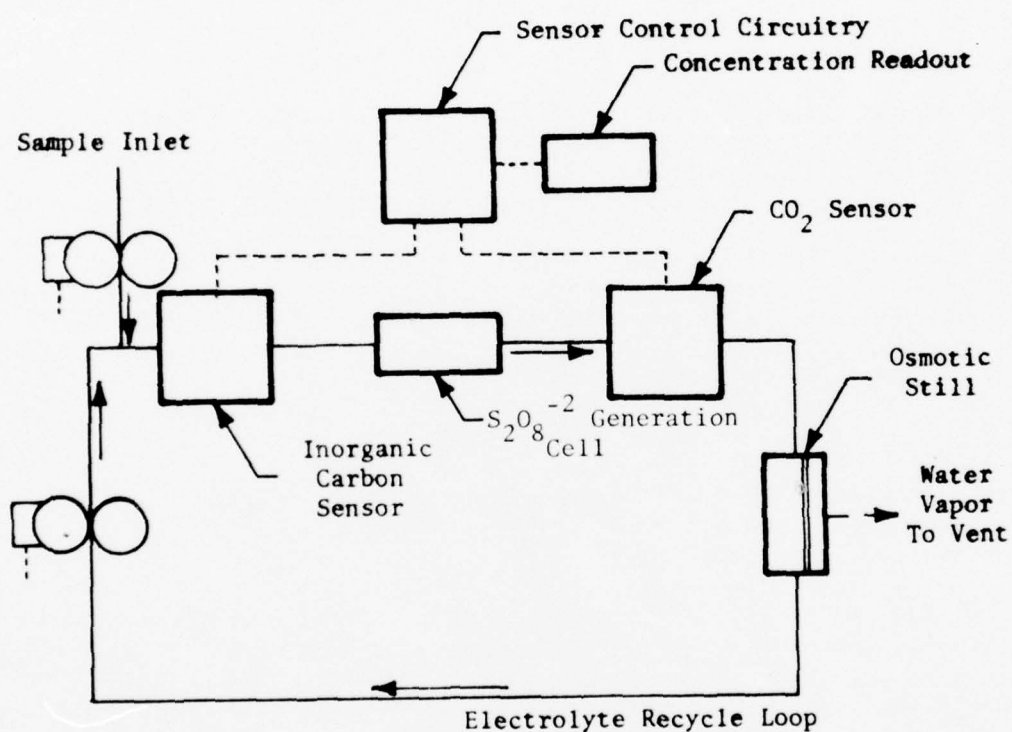


FIGURE 2 ELECTROCHEMICAL TOC ANALYZER SCHEMATIC

The membrane type pCO_2 electrode was selected for use in the analyzer because of its response characteristics, small size, reliability and low cost. The dual sensor approach was selected for the conceptual design because it permits the correction of analyzer response to inorganic carbon without the use of reagents or compressed gases. It avoids the problem of loss of volatile organics from the sample that would result if the sample was sparged to remove inorganic carbon. However, a workable alternative for the double sensor approach is the use of a membrane stripper to eliminate inorganic carbon. This device removes it by allowing inorganic carbon, converted to CO_2 by the acidic electrolyte, to diffuse from the electrolyte through a permeable membrane into a less acidic solution on the other side. The membrane stripper has been tested by Life Systems and has been found to be practical and effective. Therefore, it may be selected for use in advanced versions of the analyzer.

The results of the analysis of the Electrochemical COD and TOC Analyzers are summarized in Table 1. The analytical, system and physical parameters of the analyzers were quantified by analysis of the individual components of the analyzers, and the resulting data shows that the Electrochemical COD and TOC Analyzers are theoretically capable of providing measurements over the range of 0.5 to 30 ppm COD and 0.1 to 10 ppm TOC. The analyzers are capable of determining the organic solute concentrations with an accuracy of $\pm 10\%$ at the concentration limits for nonconsumptive reuse in the MUST hospital. The analyzers may be packaged within a volume of 1.3 ft³, and it is anticipated that they would weigh approximately 70 lb.

Program Organization

To achieve the objectives of developing and evaluating the essential components of the Electrochemical COD and TOC Analyzers, the program was divided into seven technical and management tasks:

- 1.0 Design, fabricate, assemble and test a breadboard electrochemical cell for generation of persulfate.
- 2.0 Design, fabricate, assemble and test a breadboard persulfate sensor.
- 3.0 Design, fabricate, assemble and test a breadboard pCO_2 sensor.
- 4.0 Design, fabricate and assemble Test Support Accessories (TSA) required for testing the persulfate generation cell and sensors.
- 5.0 Perform supporting research studies necessary for the design and testing of the persulfate generation cell.
- 6.0 Prepare and submit the program's documentation and data requirements.
- 7.0 Perform program management needed to successfully meet the program's cost, schedule and technical performance objectives.

TABLE 1 PRELIMINARY DESIGN GOALS AND SPECIFICATIONS

<u>Analytical Parameters</u>	
Range	0.5 to 30 ppm COD, 0.1 to 10 ppm TOC
Detection Limit	0.5 ppm COD 0.1 ppm TOC
Accuracy	10% ^(a)

<u>System Parameters</u>	
Temperature, C	
$S_2O_8^{2-}$ Cell	25
Osmotic Still	80 to 100
Flow Rates, ml/min	
Sample	0.2
Electrolyte	0.2
Power Consumption, W	300

<u>Physical Parameters</u>	
Dimensions, in (H x W x D)	12 x 12 x 16
Volume, ft ³	1.3
Weight, lb	70

^(a) At 10 ppm COD or 5 ppm TOC.

PERSULFATE GENERATION CELL

The breadboard persulfate generation cell was tested to evaluate the concept of in situ electrochemical generation of persulfate in the Electrochemical COD and TOC Analyzers. The testing was preceded by an investigation designed to identify the optimum electrolyte to be used in the cell and later in the analyzers.

Electrochemical Generation of Persulfate

Persulfate can be generated electrochemically by oxidation of SO_4^{-2} at platinum (Pt) anodes (Equation 1).⁽³⁾ The concentration of SO_4^{-2} and certain cations affect the efficiency of the generation.^(4,5) Solutions containing large concentrations of SO_4^{-2} are particularly effective since SO_4^{-2} is the reacting species. However, in acidic solutions an equilibrium between SO_4^{-2} and bisulfate (HSO_4^-) determines the actual concentration of SO_4^{-2} :



It has been determined that the concentration of SO_4^{-2} reaches a maximum of 2 M when, in the case of H_2SO_4 , the total electrolyte concentration is 5.0 M.^(3,4)

The effect of ammonium (NH_4^+), sodium (Na^+), and hydrogen (H^+) cations is demonstrated in Figure 3. Except at very large current densities, solutions containing NH_4^+ result in greater persulfate generation efficiencies than solutions containing other cations. Therefore, ammonium bisulfate (NH_4HSO_4) was selected as the electrolyte for use during the testing program. The concentration of 5.0 M was selected since the concentration of SO_4^{-2} in the solution is a near maximum concentration of 2 M.

The exact concentration of SO_4^{-2} is dependent on the temperature of the solution because of the influence of temperature on the equilibrium shown in Equation 3. The SO_4^{-2} concentrations at 0, 25 and 50°C are shown in Figure 4. Since the SO_4^{-2} concentration increases at low temperatures, low temperatures improve the efficiency of persulfate generation.

At ambient temperatures, the current efficiency for persulfate generation can be 60% if the SO_4^{-2} concentration is 2.0 M (5.0 M NH_4HSO_4) and the current density is 1.0 A/cm² (Figure 5). Lower current densities result in lower current efficiencies. This results because O_2 evolution (Equation 4), which is the major anode reaction that competes with persulfate generation, is inhibited at high current densities.



When the O_2 evolution is inhibited, persulfate generation is facilitated.

Breadboard Persulfate Generation Cell

The persulfate generation cell (shown in Figure 6) was designed to operate with 5 M NH_4HSO_4 electrolyte at a current density of 1 A/cm². The anode is a

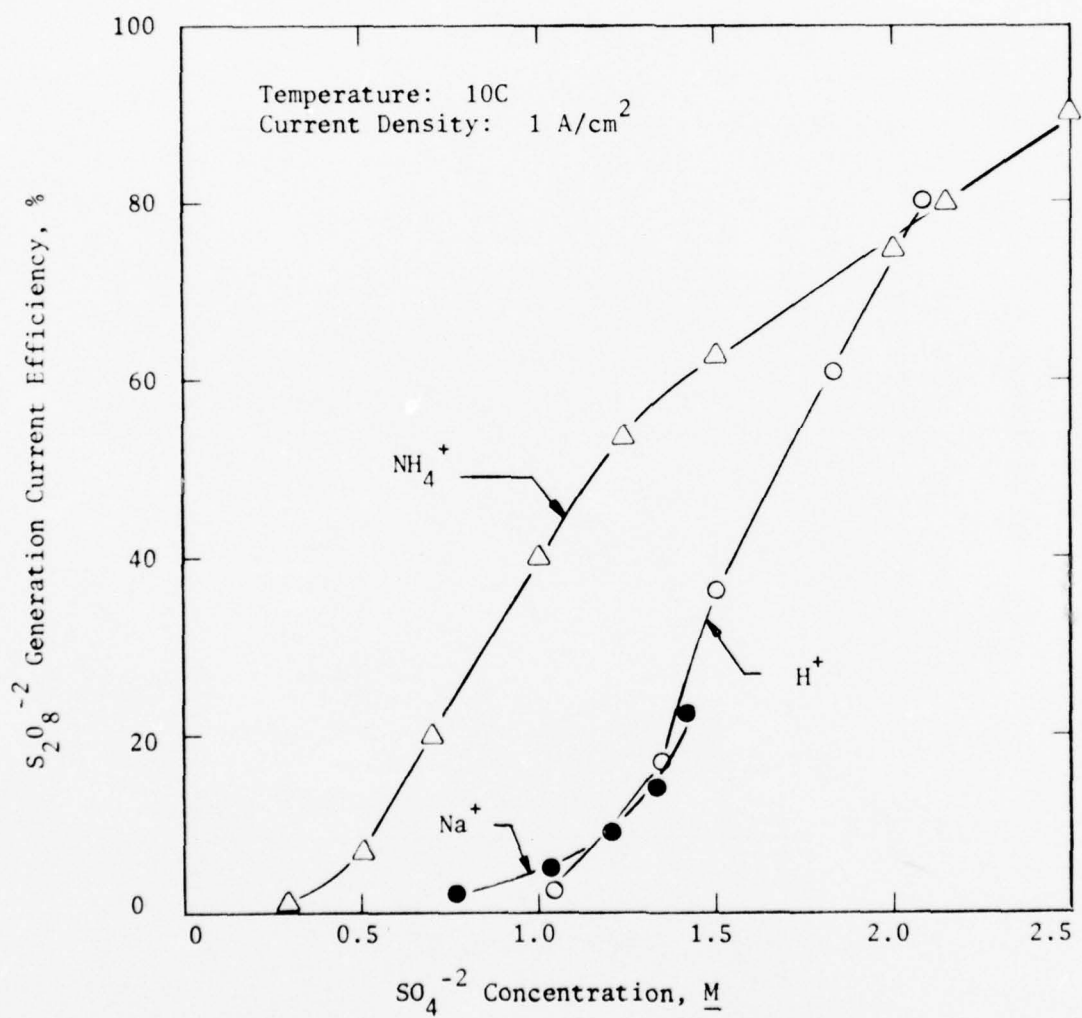


FIGURE 3 CATION EFFECT ON PERSULFATE GENERATION

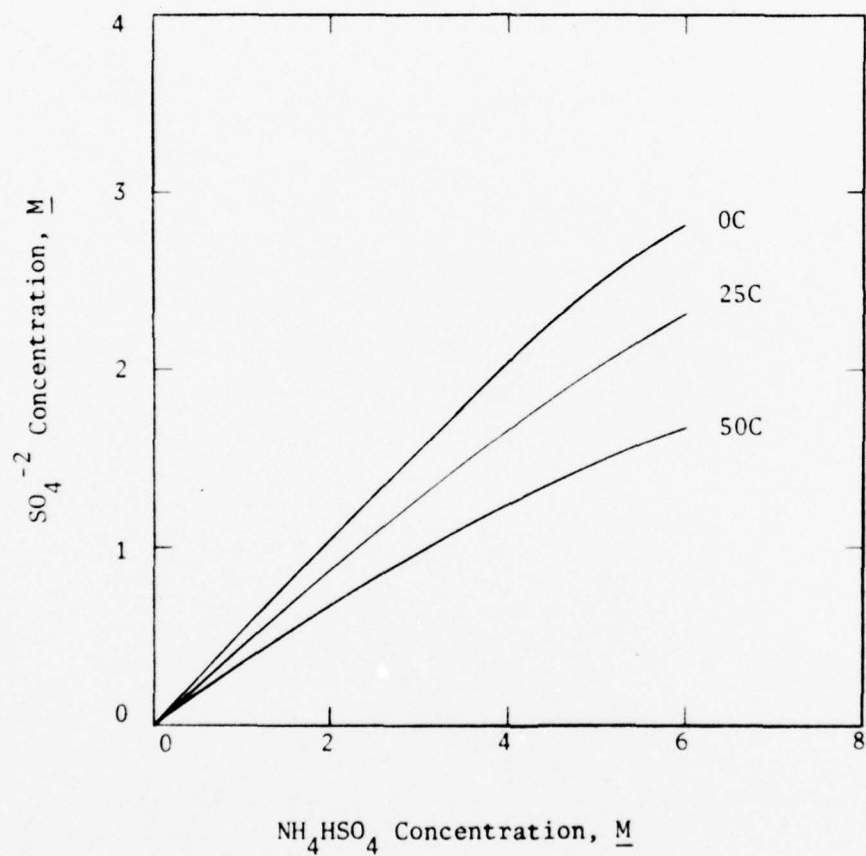


FIGURE 4 CONCENTRATION OF SULFATE IN AMMONIUM BISULFATE SOLUTIONS

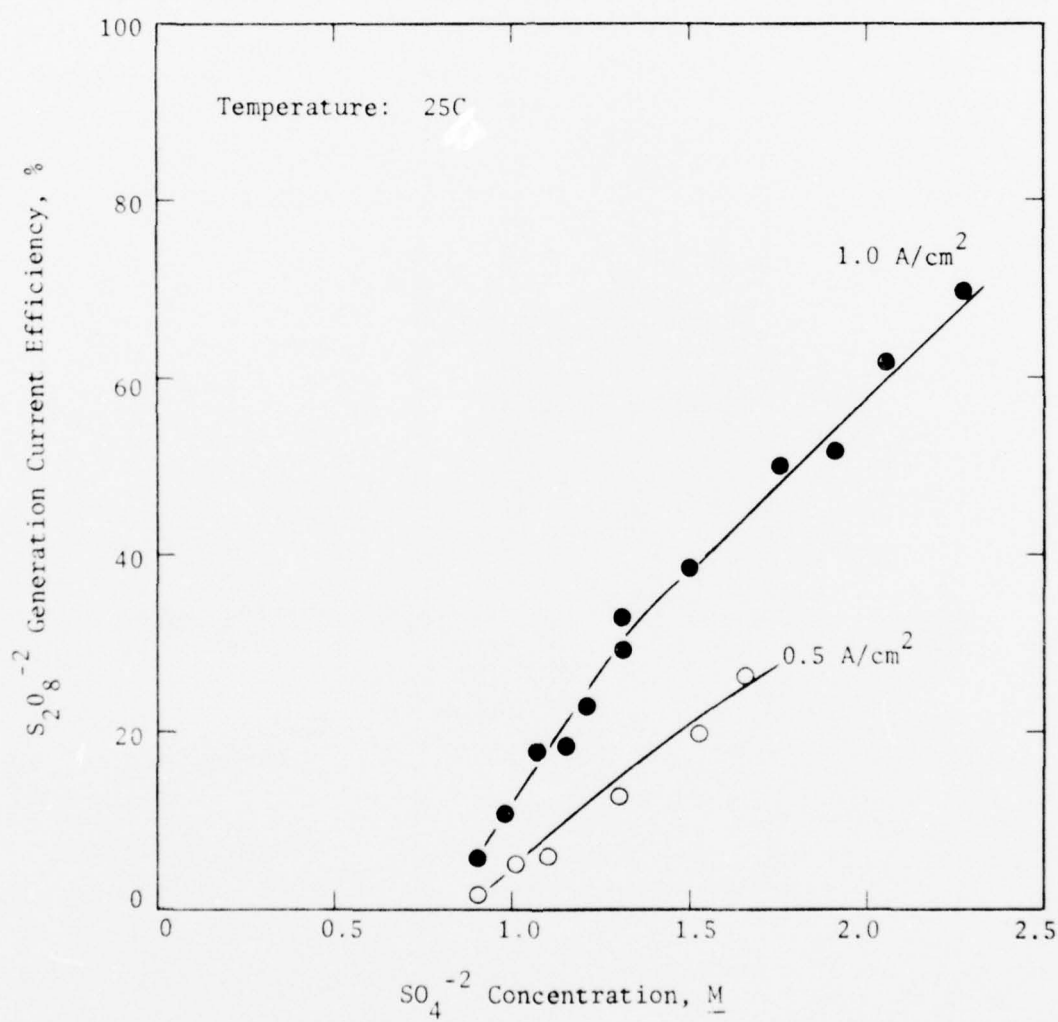


FIGURE 5 CURRENT EFFICIENCY FOR PERSULFATE GENERATION

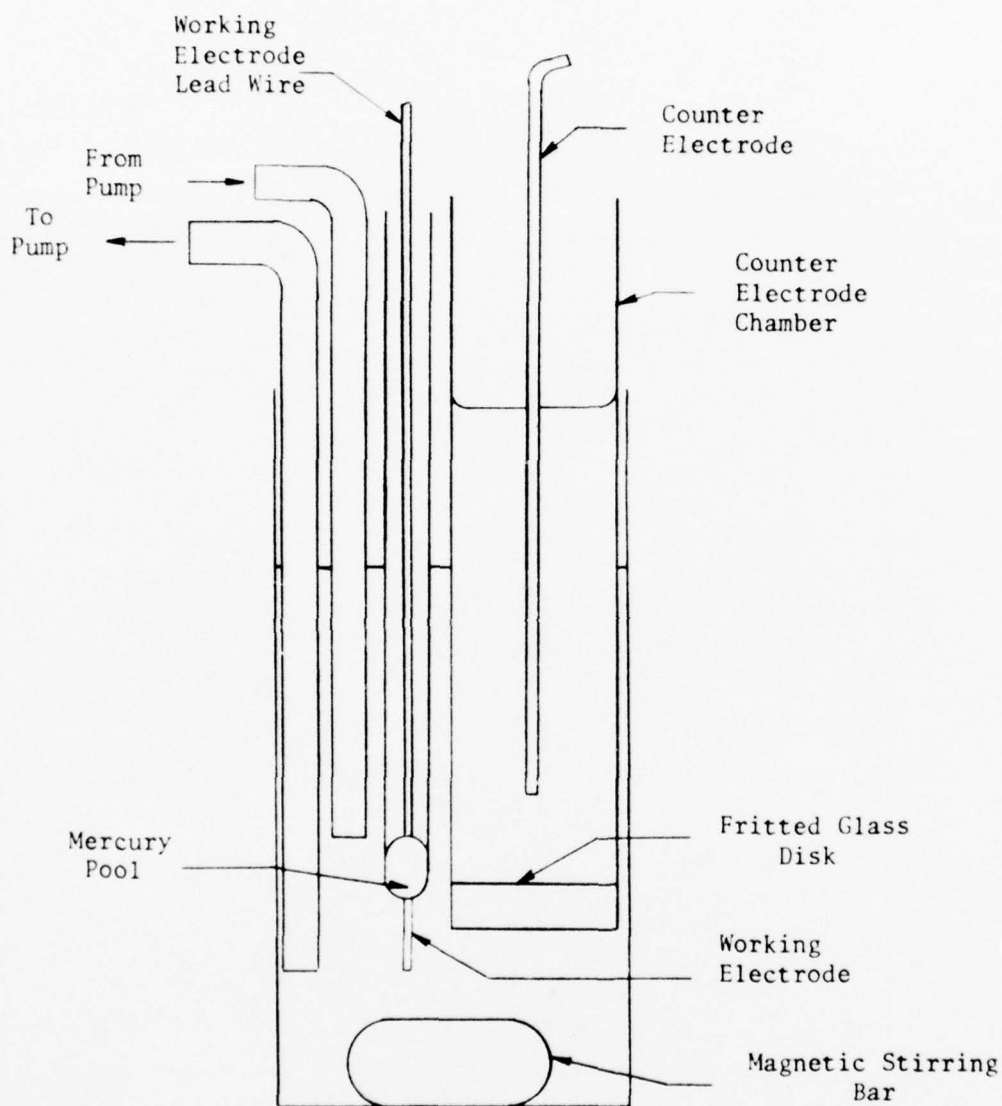
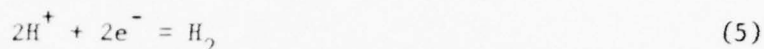


FIGURE 6 BREADBOARD PERSULFATE GENERATION CELL

Pt wire having an apparent surface area of 0.079 cm^2 . The wire is sealed in a glass tube, and electrical contact is made to the wire through a mercury (Hg) pool in the bottom of the tube.

The cathode is also a Pt wire, but it is separated from the bulk of the solution in the cell by a fritted glass disk. This separation avoids reduction of persulfate at the cathode. The main reaction at the cathode is evolution of hydrogen (H_2), as shown below.



The electrolyte is transported through the cell at a flow rate of 1.0 ml/min by a two-channel peristaltic pump. The electrolyte enters and exits the cell through the tubes shown in Figure 6. The electrolyte in the cell is stirred by a magnetic stirring bar to insure homogeneity within the cell. The current is supplied to the cell by standard 20 V/1.5 A power supply.

Persulfate Cell Test Program

The persulfate generation cell test program was designed to quantify its performance and provide data that will be useful later when the cell is integrated into the Electrochemical COD and TOC Analyzers.

Checkout Test

The initial checkout of the cell was carried out to test the functional performance of the cell, power supply and pump. During the test, bubbles of O_2 and H_2 were generated at the anode and cathode, respectively. The bubbles did not build up on the electrode surfaces because of the vertical orientation of the wire electrodes.

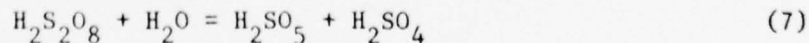
When the cell is operated at currents above 200 mA (2.5 A/cm^2) ozone (O_3) is generated at the anode and ammonia (NH_3) is evolved in the cathode chamber. The NH_3 is liberated because consumption of H^+ at the cathode shifts the equilibrium shown in Equation 6 to the right and produces NH_3 vapors.



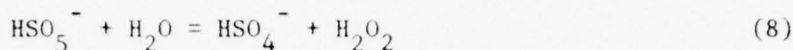
Neither O_3 nor NH_3 are produced in significant quantities when the cell is operated at the lower currents normally used.

Persulfate Generation Test

The ability of the cell to generate persulfate was quantified during this test. Also, the concentrations of other oxidizing agents that may be produced as side reactions in the cell were determined. These by-products are hydrogen peroxide (H_2O_2) and peroxomonosulfuric acid (H_2SO_5). Peroxomonosulfuric acid (also known as Caro's acid) is produced either directly at the anode⁽³⁾, or results from the decomposition of persulfate as shown below.⁽⁶⁾



Hydrogen peroxide is produced by hydrolysis of H_2SO_5 , as shown in Equation 8. (7)



The analytical method used to measure the concentrations of these species is a spectrophotometric one. In this procedure, the total oxidizing power of the solution is first measured by reacting a volume of the solution with ferrous (Fe^{+2}) salts. The total oxidizing power is the total concentration of persulfate, H_2O_2 and H_2SO_5 in the solution. Oxidation of Fe^{+2} produces ferric (Fe^{+3}) species, which are measured photometrically at 304 nm. Hydrogen peroxide is determined in a second sample by reaction with ceric (Ce^{+4}) ions after reduction of H_2SO_5 with arsenious oxide (As_2O_3). Persulfate in that sample then is determined by oxidation of Fe^{+2} . Peroxomonosulfuric acid is calculated by difference.

Using this spectrophotometric technique, the composition of the effluent of the persulfate generation cell was determined. Figure 7 shows the concentration of each species, plus the total oxidizing power, as a function of the cell current. The concentrations of H_2O_2 and H_2SO_5 are very low for all cell current values. The concentration of persulfate reaches a maximum of 0.0414 M at 335 mA (4.2 A/cm²).

Concentrations of persulfate required in the Electrochemical COD and TOC Analyzers can be calculated. If the flow rate used during testing of the persulfate generation cell (1.0 ml/min) is considered, then 1.9×10^{-3} M persulfate is required to oxidize 30 ppm COD. If methanol is the solute considered, then 2.5×10^{-3} M persulfate is required to oxidize 10 ppm TOC. However, the oxidation may occur with greater efficiency if an excess of persulfate is present in the solution to force the reaction to completion. A tenfold excess is anticipated to be sufficient for quantitative oxidation of organic solutes.

In Figure 7, the concentration of persulfate required to oxidize 30 ppm COD is shown as the lower dashed line. The upper line represents the tenfold excess concentration for oxidation of 10 ppm TOC (2.5×10^{-2} M persulfate). The persulfate generation cell is capable of generating almost twice this amount, and therefore has more than enough capacity for use in the analyzers. Normal operation will probably require cell currents around 100 mA, and this current was selected as the baseline value for subsequent tests.

The current efficiency for generation of persulfate reaches a maximum of 60% at a current of 100 mA, as shown in Figure 8. At lower currents, the efficiency decreases because of the competing evolution of O_2 , while at larger currents the evolution of O_3 is excessive. Also demonstrated in Figure 8 is the fact that above cell currents of 20 mA the concentration of persulfate is more than 95% of the total oxidizing power of the solution. At the baseline current of 100 mA, persulfate is almost the only oxidizing agent generated in the cell.

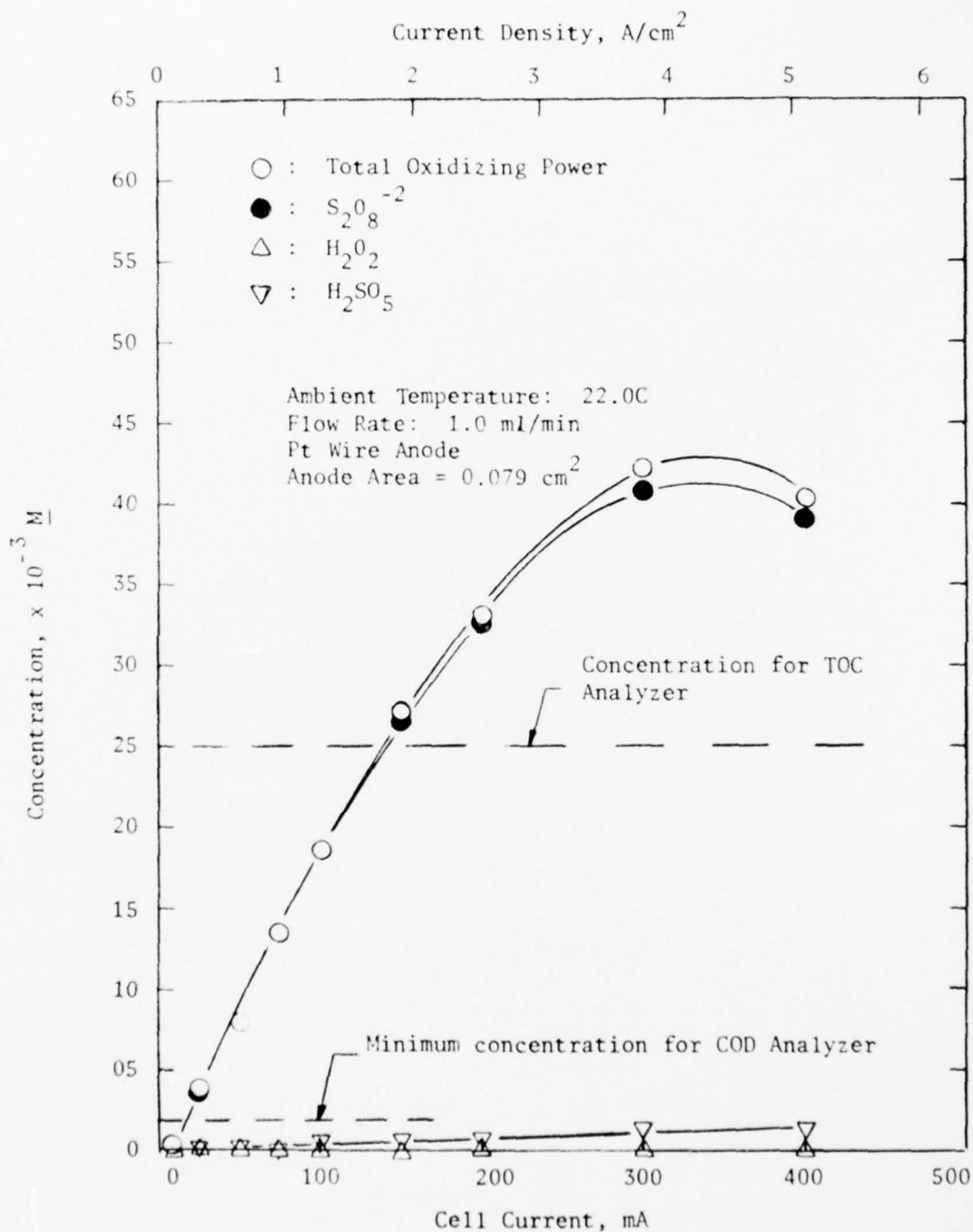


FIGURE 7 COMPOSITION OF PERSULFATE GENERATION CELL EFFLUENT

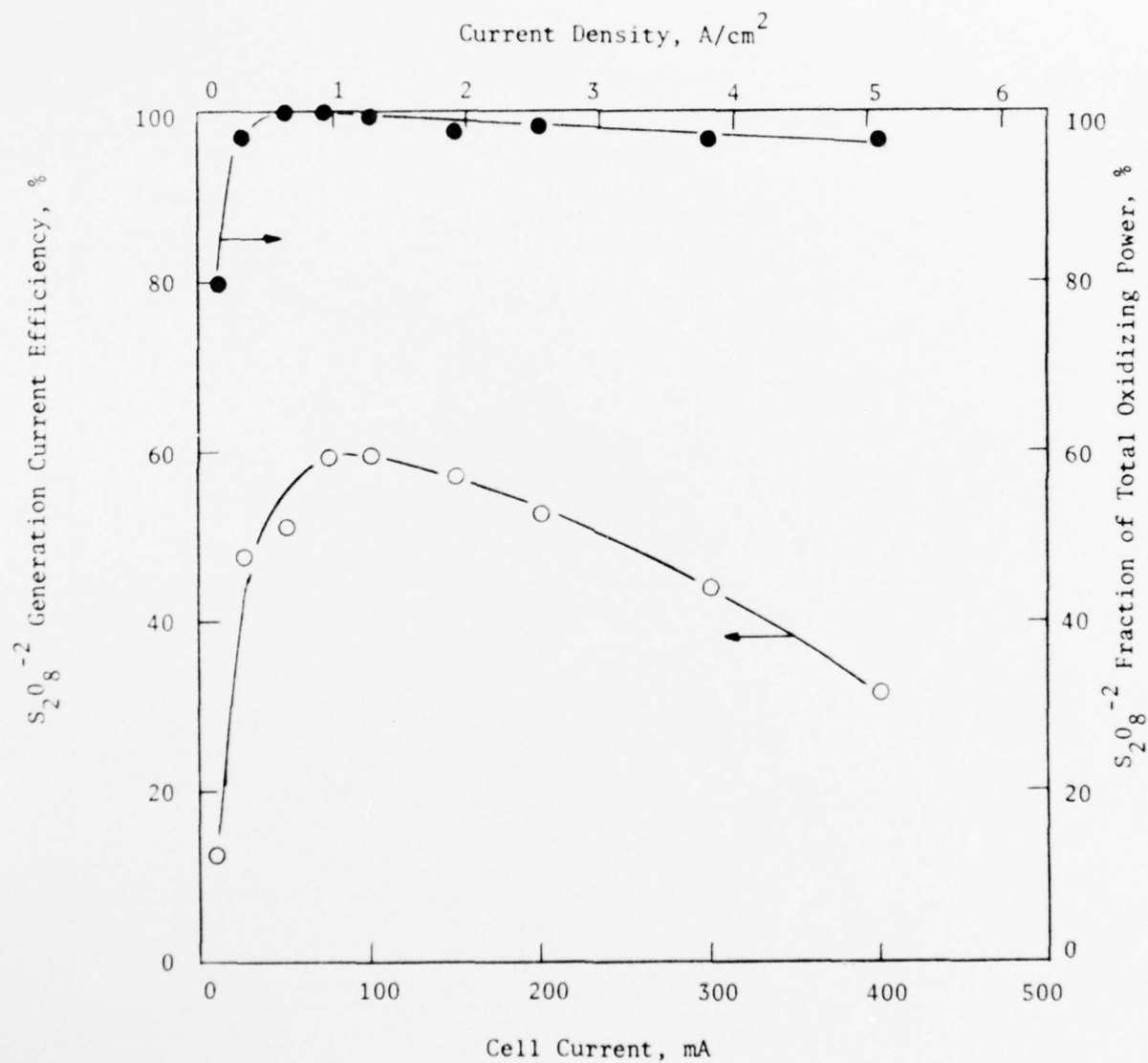


FIGURE 8 EFFICIENCIES OF PERSULFATE GENERATION

Temperature Study

The temperature effects on persulfate generation were quantified with the breadboard cell by immersing the cell in a controlled temperature water bath. As expected on the basis of the prior investigations of the persulfate generation process, lower temperatures facilitate generation of persulfate (Figure 9). However, even at 35°C, adequate persulfate is generated for use in the analyzer. Therefore, no special cooling will be required in the analyzer to maintain the cell in a temperature range for proper performance. Also, the effects of temperature changes on persulfate generation efficiency can readily be compensated for by small adjustments in the cell current.

Flow Rate Study

The efficiency for generation of persulfate at the concentration required by the analyzers is greatest in the breadboard cell when the flow rate is 1.0 ml/min. This is demonstrated in Figure 10, in which the concentration of persulfate is plotted versus a normalized cell current value (current/electrolyte flow rate). The normalized current is used because the current must be increased as the electrolyte flow rate increases in order to maintain a fixed persulfate concentration. If the efficiency of generating persulfate was constant at all flow rates, the three curves would be superimposed.

The difference in efficiency results because the cell operates at different current densities for each flow rate. The effect of current density on persulfate current efficiency has been noted (Figure 8). With the breadboard cell, operation at a flow rate of 1.0 ml/min results in current densities around the optimum of 1 A/cm². However, flow rates of 0.1 ml/min require currents in the less efficient range around 0.1 A/cm². A flow rate of 10 ml/min requires current densities around 10 A/cm². With the breadboard cell, operation at very high current densities was limited by the resistance of the counter electrode chamber frit and the 20 V limit of the power supply.

This test points out the importance of selecting the anode area for specific operating conditions to result in operation at current densities of about 1 A/cm². Larger anodes will permit operation at higher flow rates, or production of larger persulfate concentrations at the same flow rate. Therefore, the persulfate generation cell can be modified for use in many applications where widely different concentrations of organic solutes are expected.

Electrolyte Concentration Study

The electrochemical generation of persulfate is affected by the concentration of the NH₄HSO₄ electrolyte. In Figure 11, the concentration of persulfate produced with a cell current of 100 mA is shown for three concentrations of NH₄HSO₄. For 5 M NH₄HSO₄, the concentration of persulfate is 0.0186 M. The persulfate concentration decreases for both more dilute and more concentrated electrolytes. The decrease results from the lower concentration of SO₄²⁻ in the solutions.

The data shown in Figure 11 indicates that the Electrochemical COD and TOC Analyzers must have provisions for maintaining the concentration of the electro-

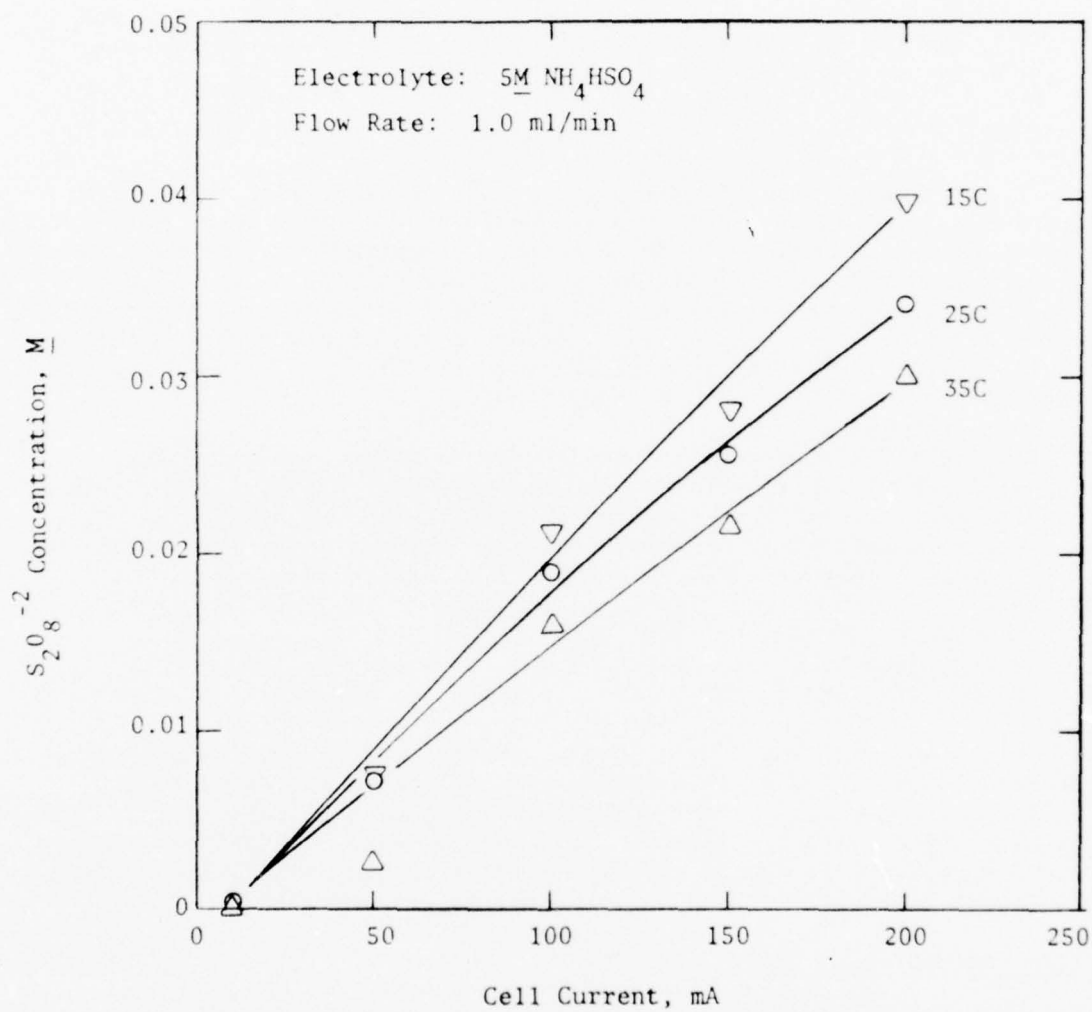


FIGURE 9 TEMPERATURE EFFECT ON PERSULFATE GENERATION

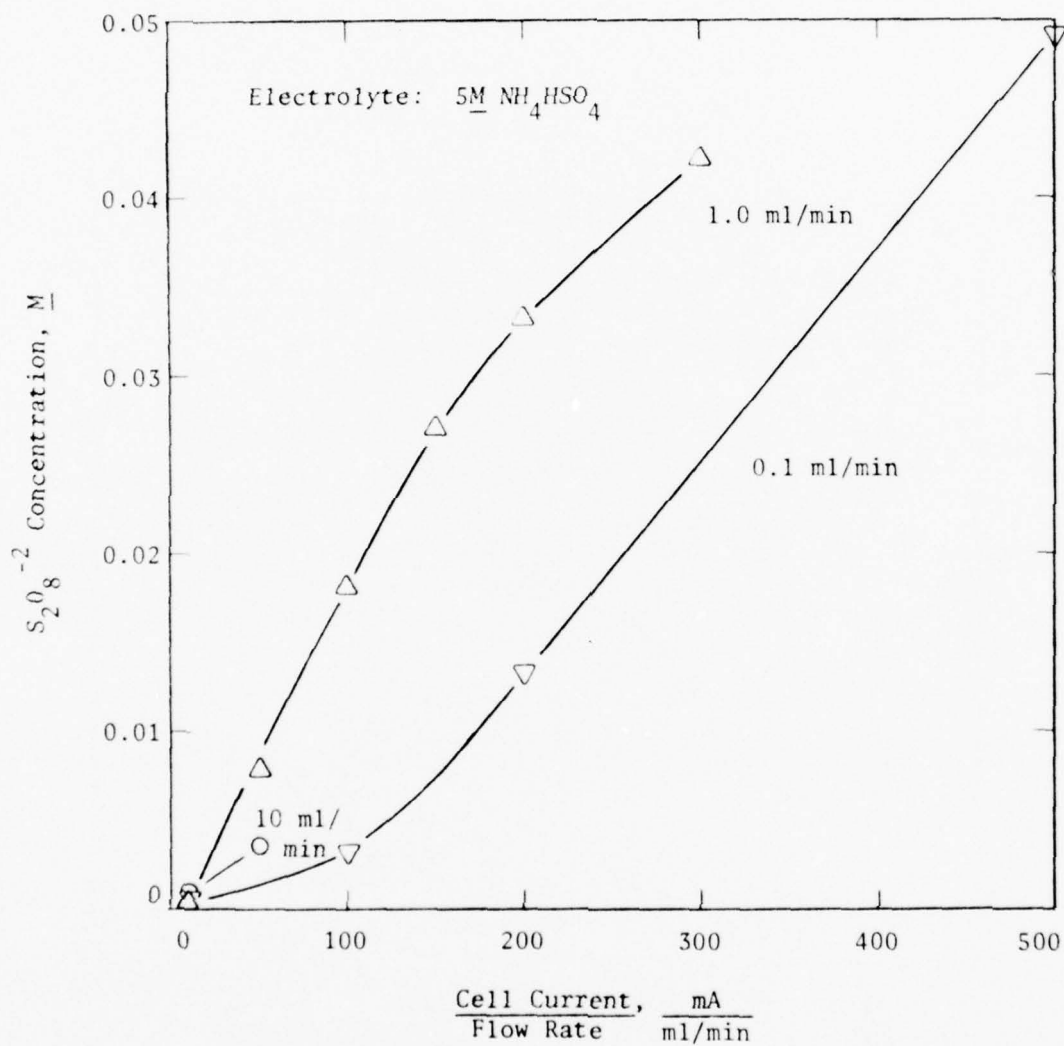


FIGURE 10 FLOW RATE EFFECT ON PERSULFATE GENERATION

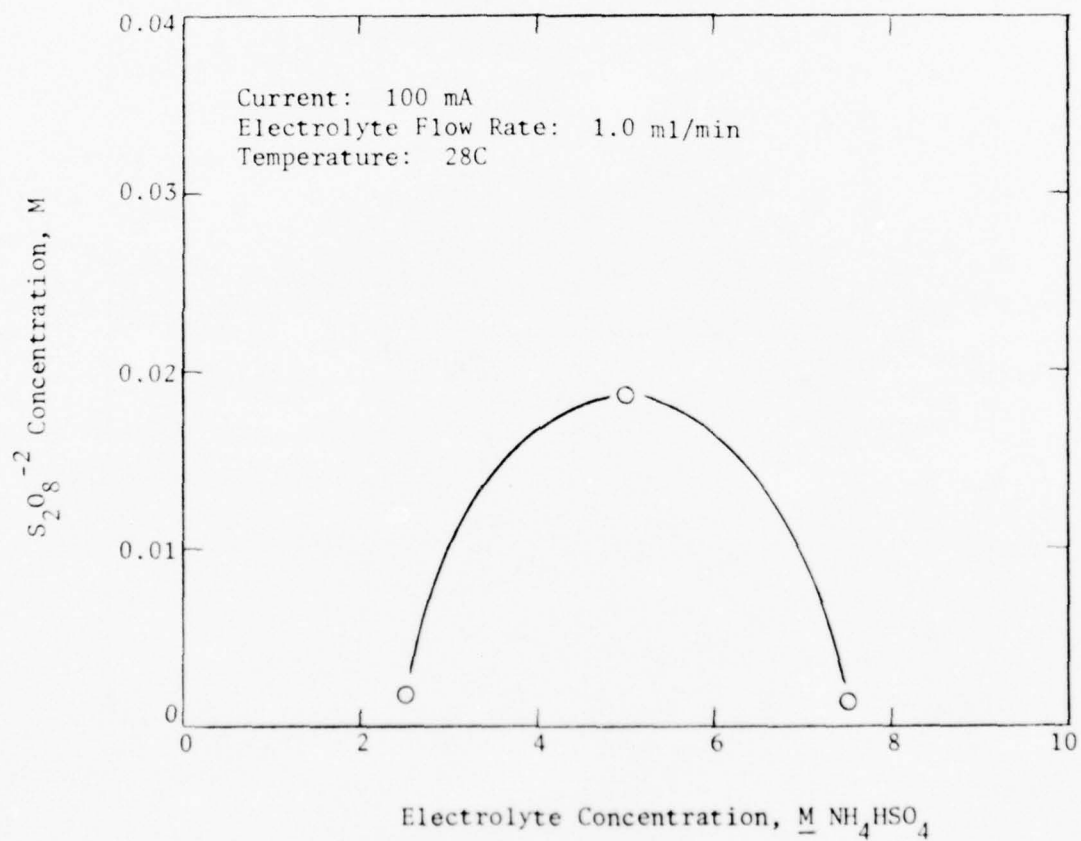


FIGURE 11 ELECTROLYTE CONCENTRATION EFFECT ON PERSULFATE GENERATION

lyte close to the value of 5 M. Maintaining the electrolyte concentration in the electrolyte recycle loop is a function of the osmotic still or other selected water elimination device. The osmotic still, therefore, must be accurately controlled to eliminate water and maintain the concentration at 5 M NH_4HSO_4 .

Interference Study

The effect on electrochemical generation of persulfate of common inorganic salts was tested. Salts were selected that the Electrochemical COD and TOC Analyzers may experience in a typical field application. The buildup of inorganic species in the electrolyte recycle loop was also addressed in this test by testing concentrations of the salts equal to those that could exist in the electrolyte recycle loop after 30 days of continuous operation.

The test considered a typical water sample containing 4.2×10^{-3} M (150 ppm) chloride (Cl_2), 7.1×10^{-4} M nitrate (NO_3^-) (10 ppm NO_3^-/N), and 5.4×10^{-6} M (0.3 ppm) Fe^{+2} . After 30 days of analyzing this solution, the electrolyte recycle loop, if its volume was 200 ml, would contain 3.6×10^{-2} M Cl_2 , 6.1×10^{-3} M NO_3^- and 4.7×10^{-5} M Fe^{+3} . Ferrous ions from the sample solution would be oxidized to Fe^{+3} by persulfate. These concentrations were used in Test No. 3, shown in Table 2. Test No. 2 used a solution with half those concentrations, and Test No. 1 was a blank, containing no interferences.

The concentration of persulfate increases from 0.169 to 0.235 M as the concentration of the interferences increases. These values are obtained with a constant cell current of 100 mA. The increased persulfate concentration results because Cl^- inhibits the competing production of O_2 at the anode.

This test demonstrates that production of persulfate is not inhibited or prevented when relatively large concentrations of salts exist in the recycle loop. Without the concentrating effect of the recycle loop, the impact of common salts found in fresh water samples is expected to be negligible. The Electrochemical COD and TOC Analyzers may require the feature of automated control of the cell current to maintain the desired persulfate concentration as inorganic salts build up in the electrolyte recycle loop. This feature can be readily incorporated, if required, in advanced versions of the analyzers.

Reproducibility Tests

The short-term precision and the day-to-day repeatability of the persulfate cell were quantified to determine if special provisions for maintaining constant persulfate concentrations in the analyzers would be required.

Short-Term Precision Study. During the precision study, the persulfate cell was operated continuously for 8 hours with a cell current of 100 mA. Ambient temperatures and an electrolyte flow rate of 1.0 ml/min were maintained. The concentration of persulfate in the cell effluent was measured on approximately an hourly basis.

The results of the test are shown in Figure 12. The concentration of persulfate remained within the range of 0.0163 to 0.0169 M. The cell has therefore

TABLE 2 PERSULFATE GENERATION CELL INTERFERENCE STUDY

	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
Cell Current, mA	100	100	100
NH ₄ HSO ₄ Concentration, <u>M</u>	5.0	5.0	5.0
NaCl Concentration, <u>M</u>	0	1.8×10^{-2}	3.6×10^{-2}
NaNO ₃ Concentration, <u>M</u>	0	3.0×10^{-3}	6.1×10^{-3}
FeNH ₄ (SO ₄) ₂ Concentration, <u>M</u>	0	2.4×10^{-5}	4.7×10^{-5}
S ₂ O ₈ ⁻² Concentration, <u>M</u>	0.0169	0.0222	0.0235

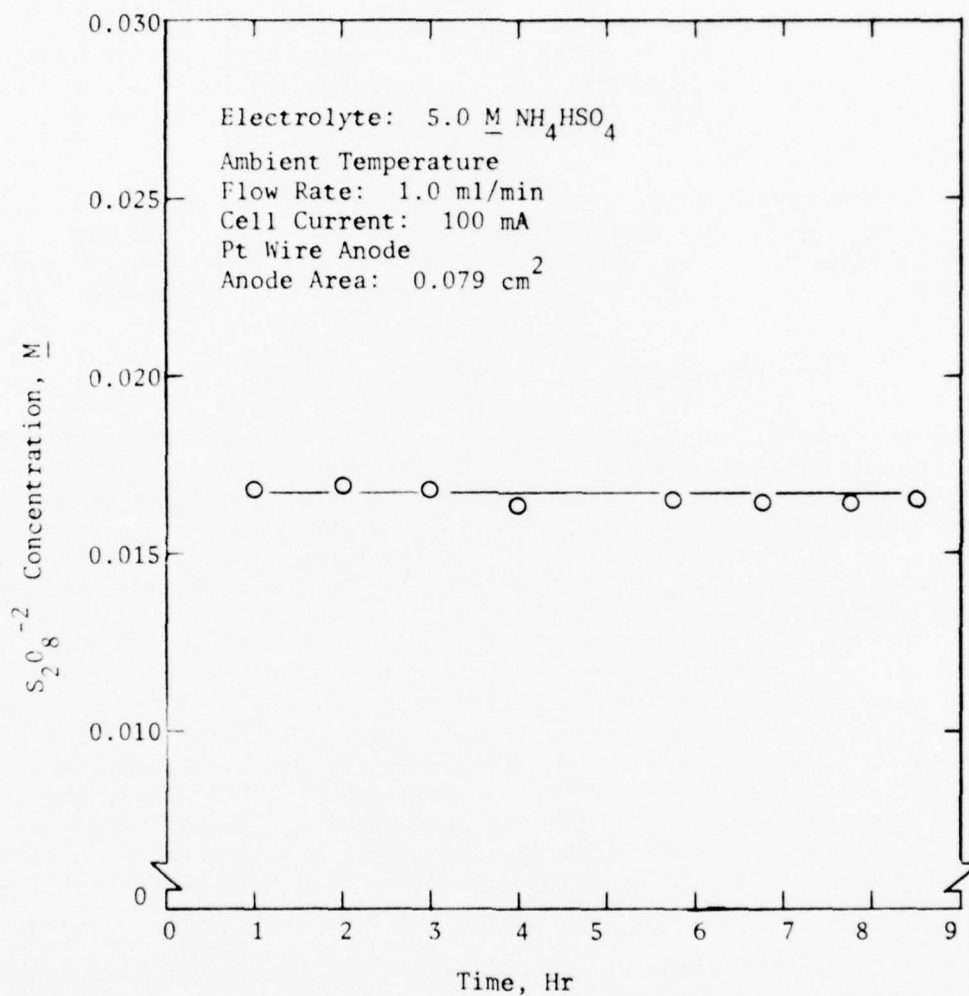


FIGURE 12 PERSULFATE GENERATION CELL
SHORT-TERM STABILITY STUDY

demonstrated excellent short-term precision, even under ambient temperature conditions.

Day-to-Day Repeatability Study. Like the precision study, the repeatability test was conducted under the conditions of 100 mA currents, an electrolyte flow rate of 1.0 ml/min, and ambient temperatures. Data points collected over widely scattered days during the testing program are shown in Figure 13. The concentration of persulfate remained within the range of 0.0166 to 0.0186 M. The lower values were obtained the last two days, during which the laboratory temperature increased to 28C. The unusually high temperature occurring those days resulted in the lower persulfate concentrations.

This test has demonstrated the potential capability of the persulfate cell to maintain a fixed persulfate concentration over a long period of time. Small cell current adjustments will be made in the analyzers to compensate for ambient temperature variations, as well as the presence of inorganic salts discussed above.

Persulfate Generation Cell Summary

The persulfate generation cell has demonstrated the ability to generate in situ the reagent required for use in the Electrochemical COD and TOC Analyzers. The effects of temperature, flow rate and electrolyte concentration variations have been quantified and found to be within acceptable limits for control or compensation of those effects. The buildup of common inorganic salts within the electrolyte recycle loop of the analyzer has been demonstrated to present no significant problem.

Good performance of the persulfate generation cell requires a relatively concentrated electrolyte (5 M NH_4HSO_4). Improved performance of the cell may therefore be obtained by repositioning it in the Electrochemical COD and TOC Analyzers. It is now located in the designs downstream of the sample injection point (Figures 1 and 2). The electrolyte is diluted by the sample there. Therefore, improved performance will probably result by repositioning the cell upstream of the sample inlet. With this modification, the cell will operate in 5.0 M NH_4HSO_4 , while the sensors and osmotic still will experience 2.5 M NH_4HSO_4 .

The analytical specifications of the persulfate generation cell are summarized along with the specifications of the sensors in a later section (see Table 7).

PERSULFATE SENSOR

The persulfate sensor will be used in the Electrochemical COD Analyzer to measure the concentration of persulfate consumed during the oxidation of organic solutes. This quantity of persulfate is proportional to the COD content of the sample.

The persulfate sensor must consume no reagents to achieve the design goal of consumption of no reagents or compressed gases by the Electrochemical COD Analyzer. For example, the spectrophotometric technique used to measure the concentration of persulfate in the generation cell effluent cannot be used because a reagent containing Fe^{2+} is consumed.

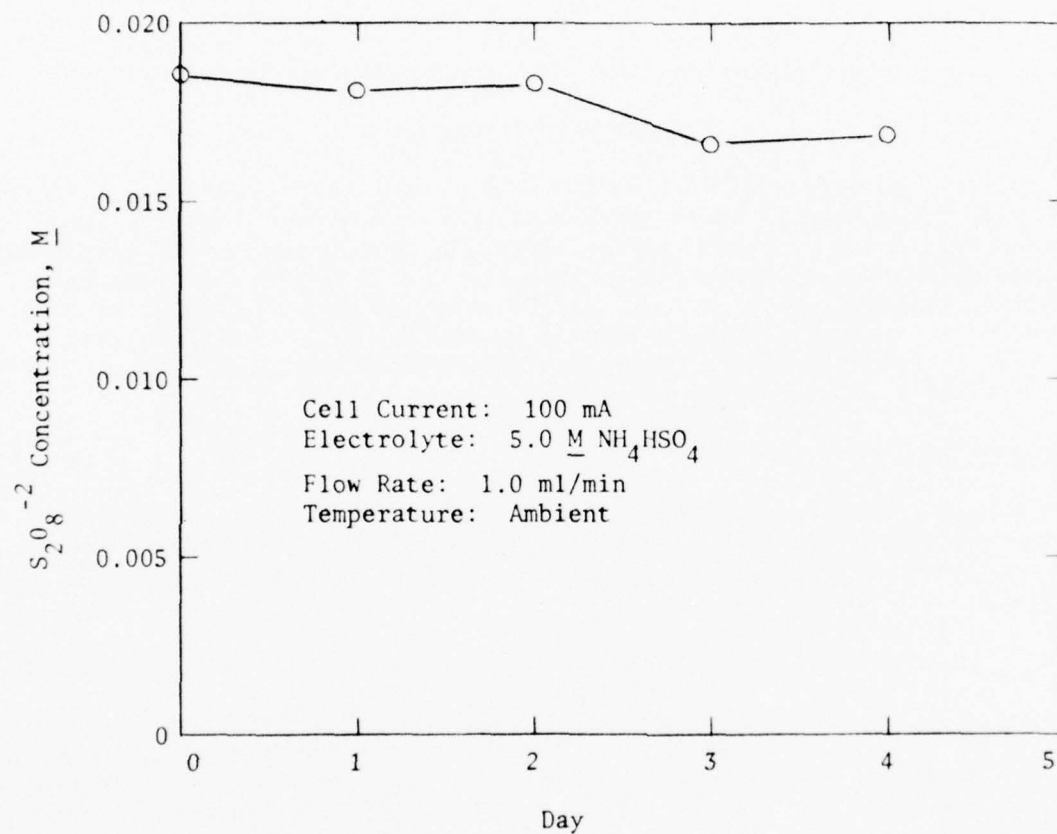


FIGURE 13 DAY-TO-DAY REPRODUCIBILITY OF
PERSULFATE GENERATION CELL

Direct spectrophotometric techniques, in which the light of a specific wavelength absorbed by the persulfate is related to its concentration, were evaluated. Persulfate weakly absorbs UV radiation, but Cl^- and NO_3^- absorb much more strongly.⁽⁸⁾ Therefore, direct spectrophotometric monitoring of persulfate would be subject to severe interferences by common salts.

Several electrochemical techniques were also evaluated since they could be used without reagents other than the electrolyte already in the analyzer. Potentiometric, amperometric and coulometric methods were investigated.

Potentiometric Methods

Potentiometric methods are based on the measurement of the potential difference between an indicating electrode and a reference electrode. The reference electrode provides a reference potential that does not change with variations in the concentration of persulfate. The potential difference between the indicating and reference electrodes may be measured with no current flowing through the indicating electrode (normal potentiometry), or with current flowing (potentiometry with a polarized indicating electrode). The performance of these methods is discussed below.

Potentiometric Sensor

Normal potentiometric techniques are the simplest electroanalytical methods to implement and are compatible with a flow-through, continuous sensor design. Therefore, the potentiometric approach was the first one evaluated for monitoring persulfate.

Figure 14 is a schematic of a normal potentiometric sensor. The indicating electrodes used during this investigation were made of Pt, gold (Au), Ag, palladium (Pd), glassy carbon, pyrolytic graphite and porous graphite. The reference electrode was a Saturated Calomel Electrode (SCE). The voltage response, E , of the sensor is the voltage difference between the indicating electrode and the SCE. The theoretical response can be calculated from the Nernst Equation, and is shown below for the case of persulfate:

$$E = E^0 + 2.303 \frac{RT}{2F} \log \frac{(\text{S}_2\text{O}_8^{2-})}{(\text{SO}_4^{2-})^2} \quad (10)$$

where E^0 = constant, V
 R = Universal Gas Constant, joules/K
 T = Temperature, K
 F = Faraday's Constant, coulombs/equivalent
 $(\text{S}_2\text{O}_8^{2-})$ = Concentration of $\text{S}_2\text{O}_8^{2-}$, M
 (SO_4^{2-}) = Concentration of SO_4^{2-} , M

The sensors did not exhibit the theoretical response predicted by Equation 10. Instead the response for all the indicating electrode materials was similar to that shown in Figure 15 for Pt. Two days of tests produced greatly different response curves. Neither curve was linear nor did they have the theoretical

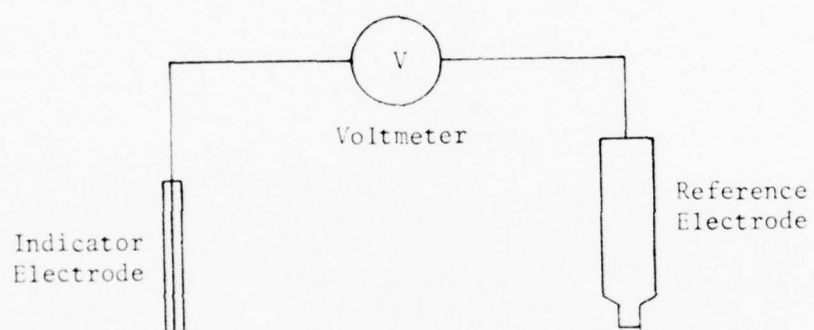


FIGURE 14 POTENTIOMETRIC PERSULFATE SENSOR

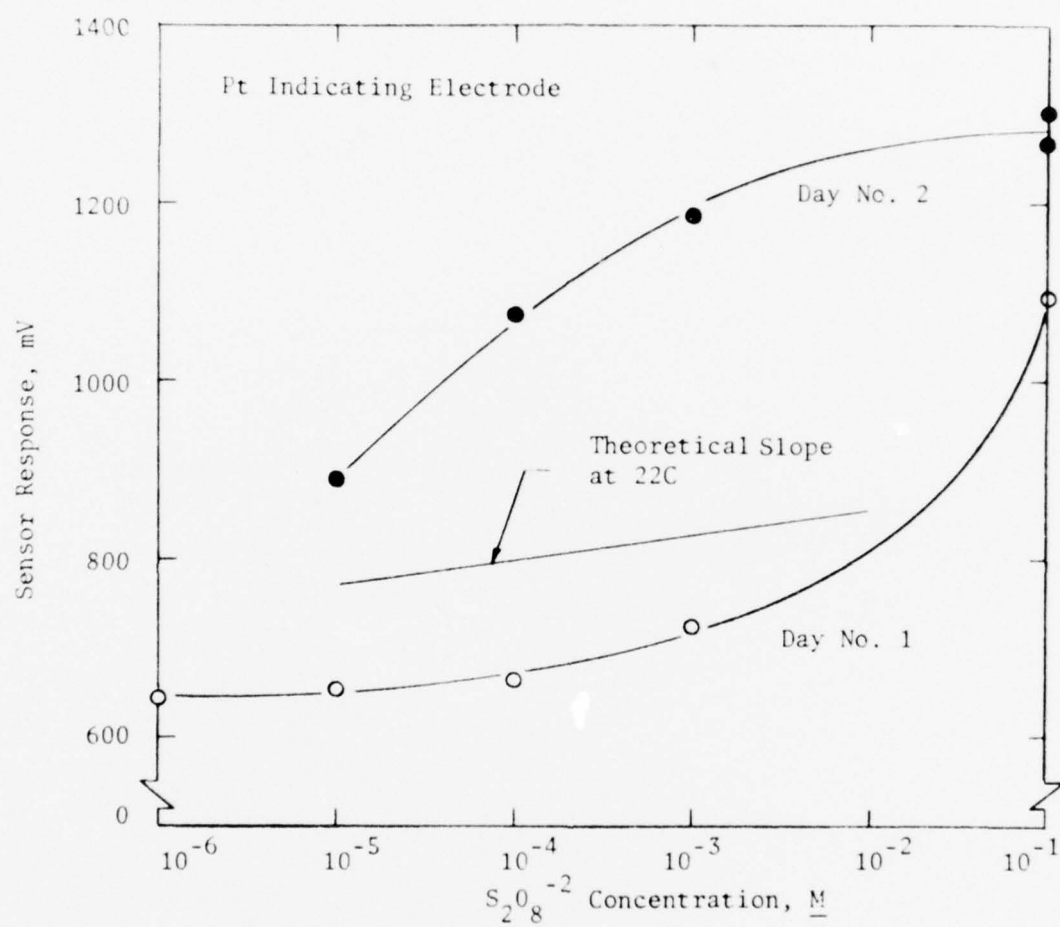


FIGURE 15 RESPONSE OF POTENTIOMETRIC PERSULFATE SENSOR

slope. The non-theoretical performance of the indicating electrodes is probably due to slow kinetics for the reaction of persulfate at the electrodes (Equation 11).



Other electrode reactions, such as reduction of O_2 (Equation 12), may also interfere.



The poor day-to-day reproducibility of the response has been attributed to electrode history effects.

These problems can sometimes be eliminated by applying a small current to the indicating electrode. The current serves to maintain the electrode in a reproducibly reduced or oxidized state, depending upon the polarity of the current. Therefore, the response to persulfate of a potentiometric sensor with a polarized indicating electrode was tested.

Potentiometric Sensor With Polarized Electrode

A three-electrode system is required for measurements using the polarized electrode potentiometric technique. Such a system is shown schematically in Figure 16. A counter electrode is added to the cell to provide a pathway for current from the indicating electrode. No current flows through the reference electrode to avoid polarizing the electrode and producing potential measurement errors.

The galvanostat/potentiostat shown in Figure 16 is capable of controlling either the current or potential of the indicating electrode. Using this technique, a small current (1 μA to 1 mA) is applied to the indicating electrode, and the voltage difference between the indicating and reference electrodes is recorded. Life Systems' Electroscan 30 and electrochemical cell used during these tests are shown in Figure 17. The indicating electrodes were of the rotating disk electrode (RDE) geometry (Figure 18), and they were mounted in Life Systems' electrode rotator shown in Figure 17. When the electrodes are rotated about their longitudinal axis, solution flows up to the face of the disk electrode in a uniform and reproducible manner (Figure 18b). A Teflon sheath insulates the sides of the electrode and stainless steel shaft which makes electrical contact to the electrode. This electrode geometry permits the electrode to be readily polished and pretreated, resulting in a reproducible electrode surface.

The most responsive indicating electrodes from the previous potentiometric evaluation were tested with the polarized electrode technique. Again, the data collected with the Pt electrode is indicative of results obtained with other electrodes. Figure 19 shows the Pt electrode behavior. The greatest response was obtained with a current of 10 μA , but poor day-to-day reproducibility was observed.

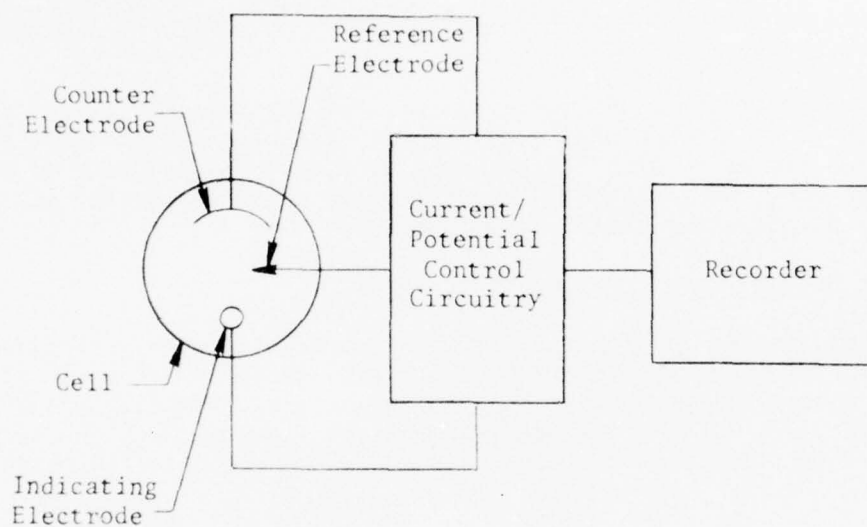


FIGURE 16 FUNCTIONAL BLOCK DIAGRAM OF
THREE-ELECTRODE GALVANOSTAT/POTENTIOSTAT

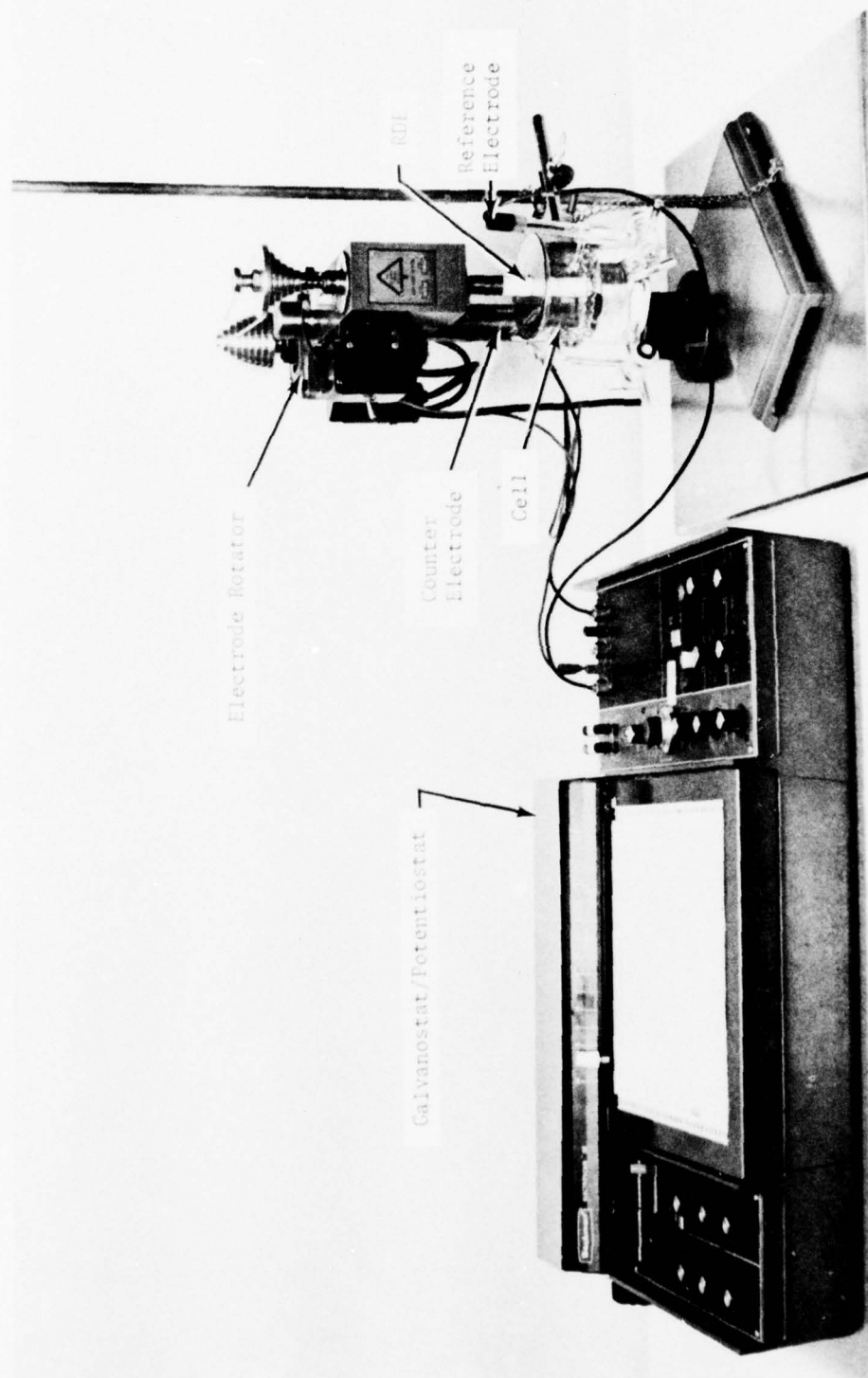


FIGURE 17 LIFE SYSTEMS THREE-ELECTRODE ELECTROANALYTICAL INSTRUMENTATION

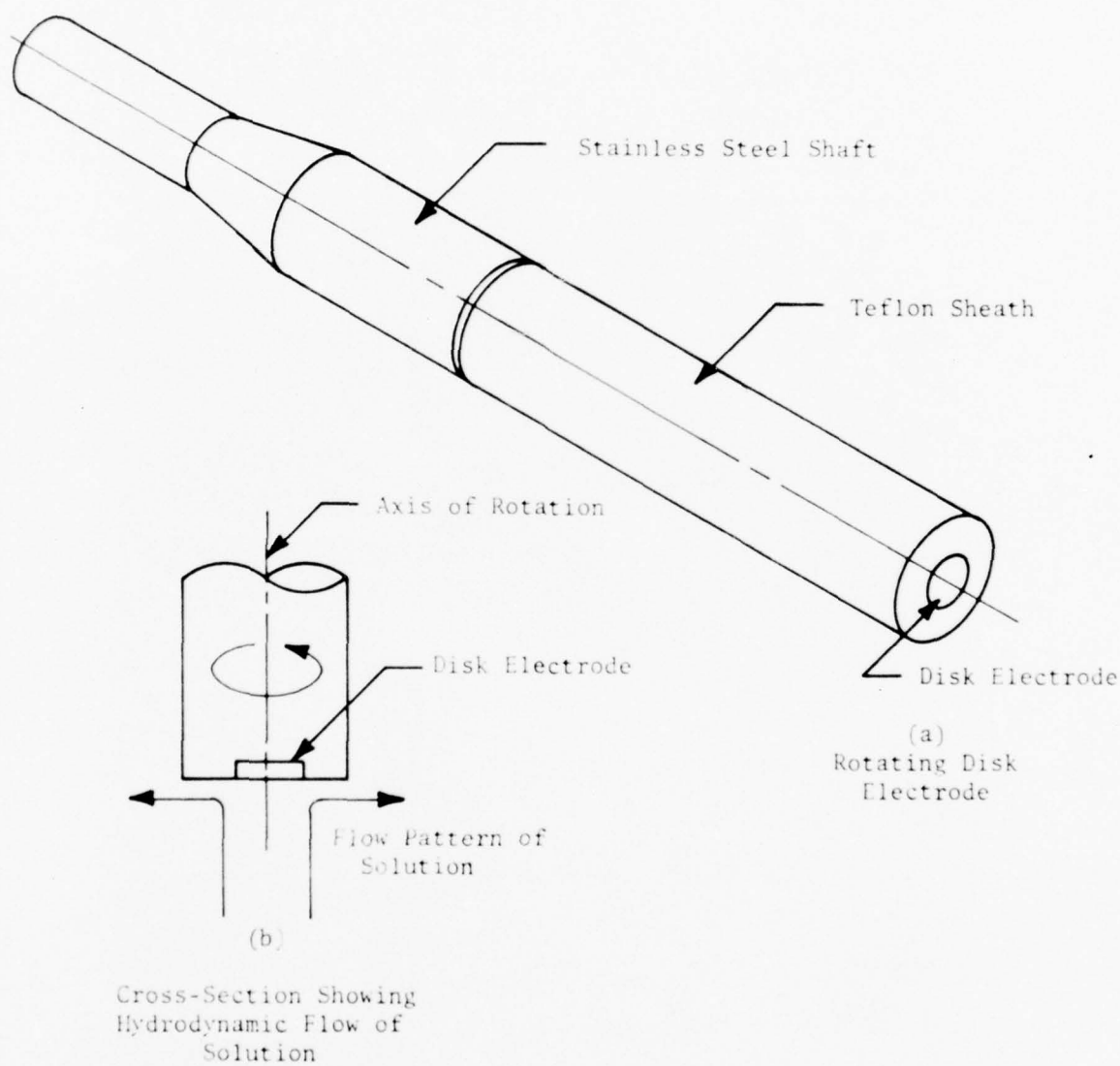


FIGURE 18 GEOMETRY AND OPERATION OF ROTATING DISK ELECTRODE

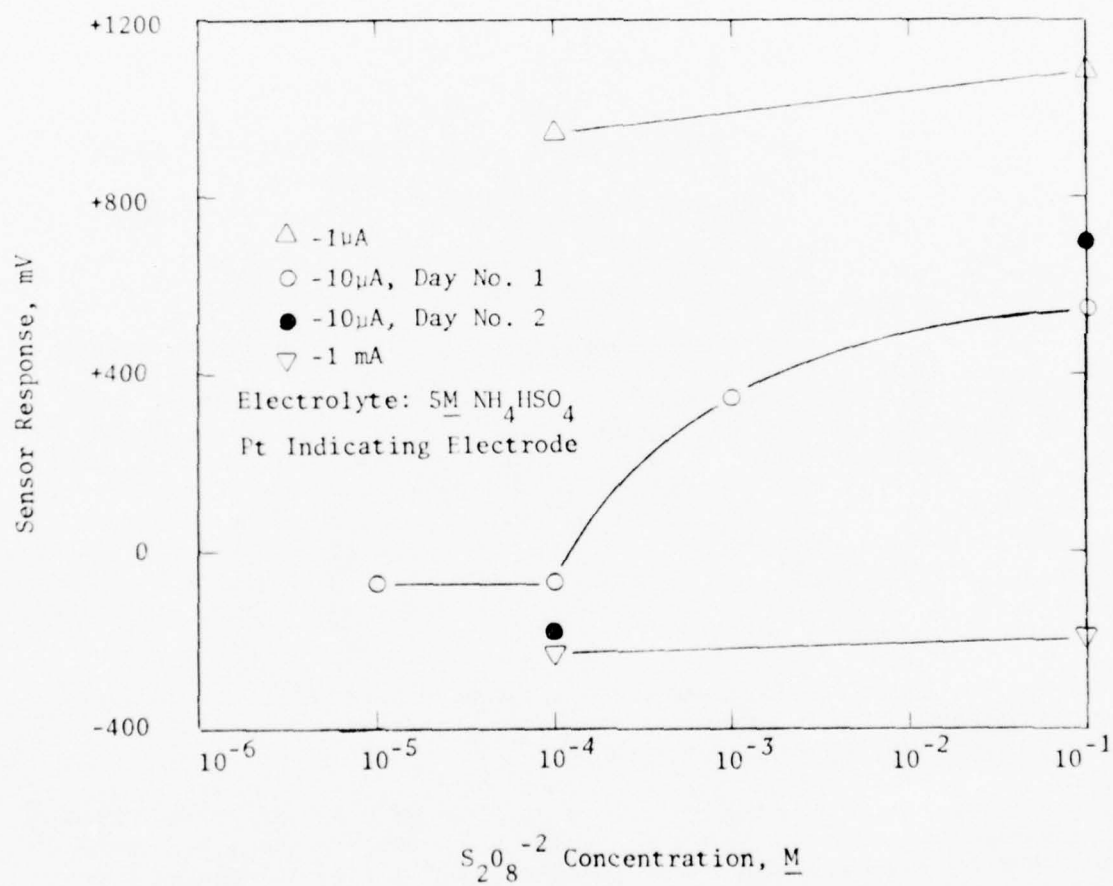


FIGURE 19 RESPONSE TO PERSULFATE OF POTENTIOMETRIC SENSOR WITH POLARIZED ELECTRODE

These results demonstrate that further development of potentiometric techniques would not result in the quality of performance required by the Electrochemical COD Analyzer. Therefore, other electrochemical techniques were evaluated.

Amperometric Method

Amperometry is the measurement of current at an indicating electrode when the potential of the electrode is controlled at a fixed value. The current results from the oxidation or reduction at the electrode of the species being determined.

A potentiostat like that shown in Figures 16 and 17 was used for the amperometric evaluation. The RDE geometry (Figure 18) was used during these tests because the relationship between electrode current and the concentration of electroactive species is well-known.⁽⁹⁾ This relationship is given in Equation 13.

$$I = 0.62 n F A D^{2/3} \nu^{-1/6} \omega^{1/2} C^b \quad (13)$$

where

I = Electrode current, mA

n = Equivalent weight per mole of electroactive species

A = Geometric area of disk electrode, cm^2

D = Diffusion coefficient of electroactive species, cm^2/sec

ν = Kinematic viscosity, cm^2/sec

ω = Rotational velocity of RDE, rad/sec

C^b = Bulk concentration of electroactive species, M

When the current at the indicating electrode is measured as a function of the applied potential, voltammograms like those shown for a Au RDE in Figure 20 result. The voltammograms in Figure 20 are of air-saturated 2.5 M NH_4HSO_4 , with and without 1×10^{-3} M persulfate. The persulfate is reduced at potentials more negative than +0.4 V versus SCE, as indicated by the large cathodic currents at those potentials obtained for the persulfate-containing solution. The reaction occurring at the electrode is that given in Equation 11. Oxygen in the solution is also shown to be reduced at these potentials, according to the reaction shown by Equation 12.

Dissolved O_2 , therefore, is a potentially serious interference. Variations in the concentrations of O_2 dissolved in the solution would result in a current variation and COD concentration error.

The two electrodes most responsive to persulfate were Au and glassy carbon. The amperometric response curves for these materials are shown in Figure 21. The Au RDE produced the most linear response, but glassy carbon was more sensitive.

Both electrodes were responsive to O_2 as well as persulfate. The response of the Au electrode to the O_2 in the air-saturated electrolyte produced a reduction current of 30 mA (Figure 20). When this current value is compared to the response of the electrode to persulfate (Figure 21), the O_2 response equals that which would be obtained from 4.8 ppm COD if the Au RDE were mounted as a sensor in the analyzer. Variations in the dissolved O_2 concentration in the water sample or electrolyte recycle loop would then produce sensor fluctuations equal to several ppm COD.

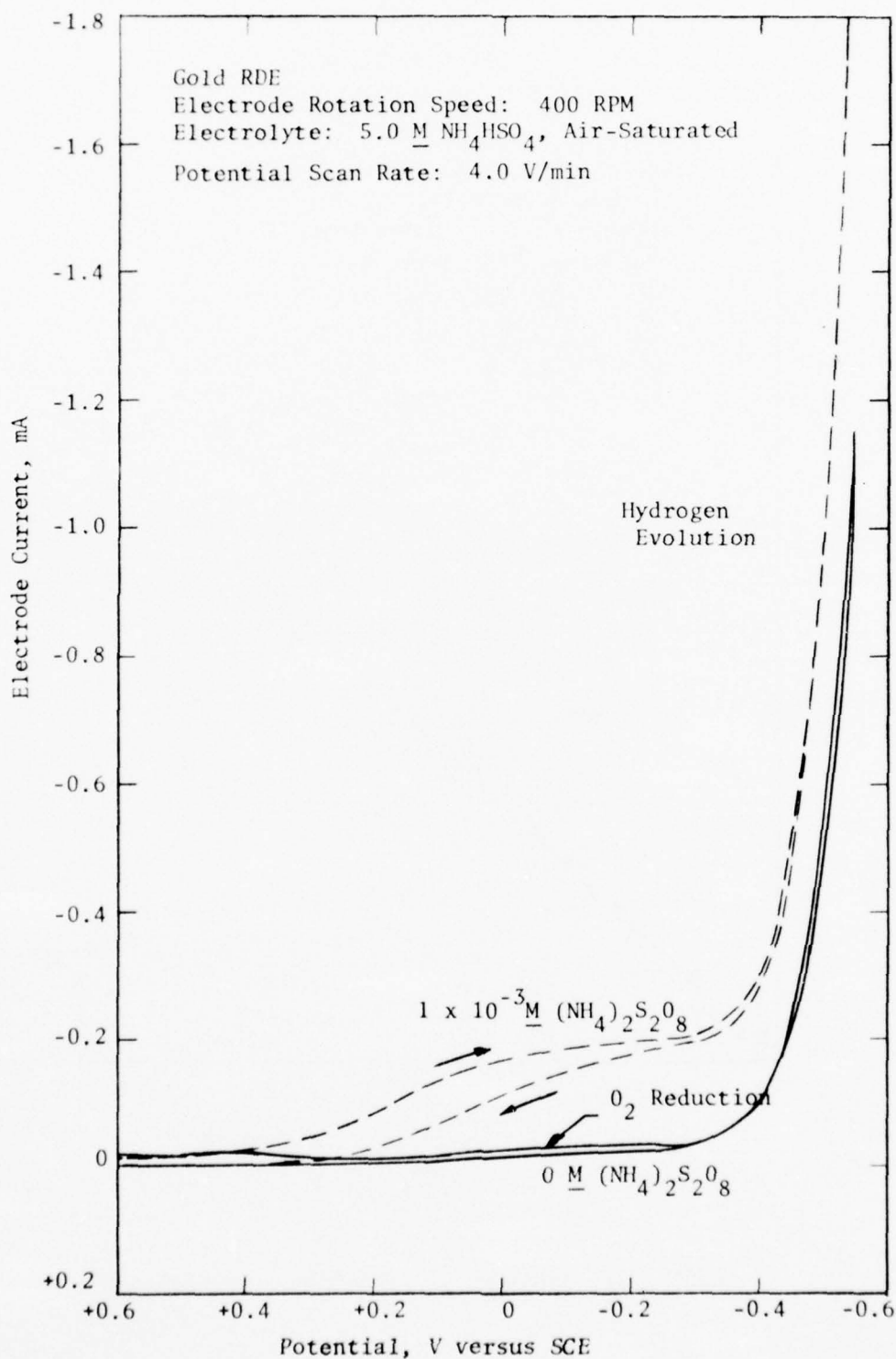


FIGURE 20 VOLTAMMOGRAM OF PERSULFATE REDUCTION

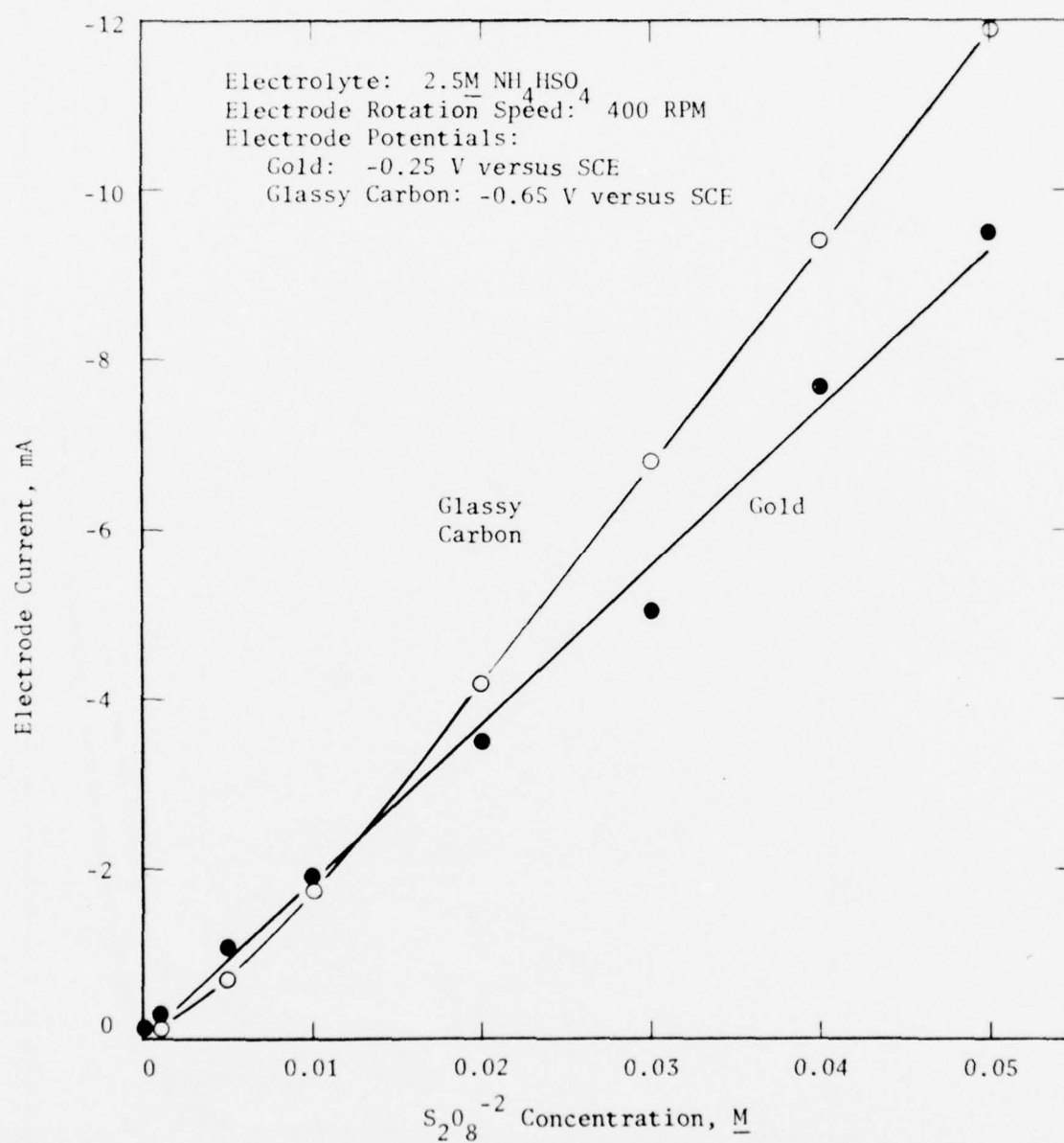


FIGURE 21 AMPEROMETRIC RESPONSE TO PERSULFATE

Because of the anticipated error from dissolved O_2 concentration variations, the third electroanalytical technique, coulometry, was investigated. This technique produced the required linear response to persulfate without errors due to the reduction of O_2 .

Coulometric Method

Coulometry is the measurement of the coulombs, Q , of charge required to oxidize or reduce electroactive species at an electrode. Coulometric techniques require batch-style sensors in which a certain volume of the test solution is added to the coulometric cell, and the electroactive species in that volume is oxidized or reduced. In this case, persulfate is reduced at a constant potential at a Hg pool electrode in the coulometric cell. The reaction is shown above in Equation 11.

Coulometric Cell

The coulometric persulfate sensor is shown schematically in Figure 22. The Hg pool electrode is contained in the bottom of the cell. Electrical contact is made by means of a small wire inserted through the cell bottom. The test solution is added to the cell and is mechanically stirred. The reference and counter electrodes are in chambers separated from the test solution by fritted disks.

The coulometric cell is controlled by a potentiostat similar to that shown in Figure 16. However, the current flowing through the Hg electrode is integrated by a coulometer used with the potentiostat.

When solution containing persulfate is added to the coulometric cell, the persulfate is reduced at the Hg electrode. The current resulting from the persulfate reduction is initially large, but decreases exponentially as the persulfate is consumed. This is shown in Figure 23. The coulometer integrates the current as a function of time during the reduction. This integral equals the coulombs, Q , of charge required for complete reduction of the persulfate added to the cell. The quantity, Q , is shown as a shaded area under the curve in Figure 23, and is related to the concentration of persulfate in the sample by Equation 14.

$$Q = \frac{FV}{500} (S_2O_8^{-2}) \quad (14)$$

where V = Volume of sample, ml

There is always a small residual current flowing through the Hg electrode even when persulfate is absent from the solution. The coulometer is automatically adjusted to integrate only currents larger than the residual current, as indicated in Figure 23.

Coulometric Response to Persulfate

The response of the coulometric sensor to persulfate is shown in Figure 24. In addition to the experimentally determined line, the theoretical response

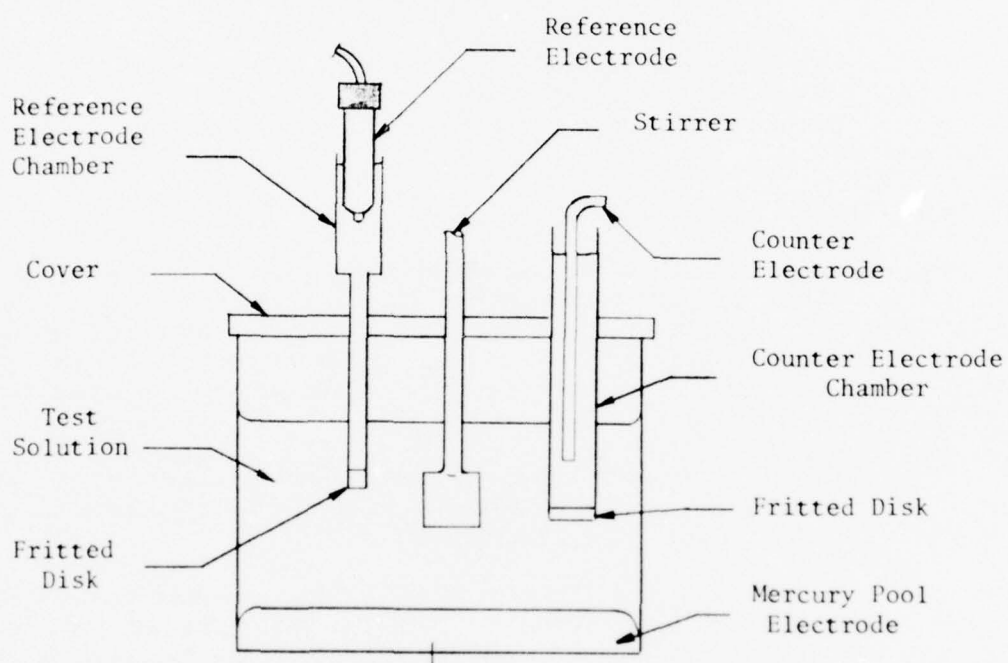


FIGURE 22 COULOMETRIC PERSULFATE SENSOR

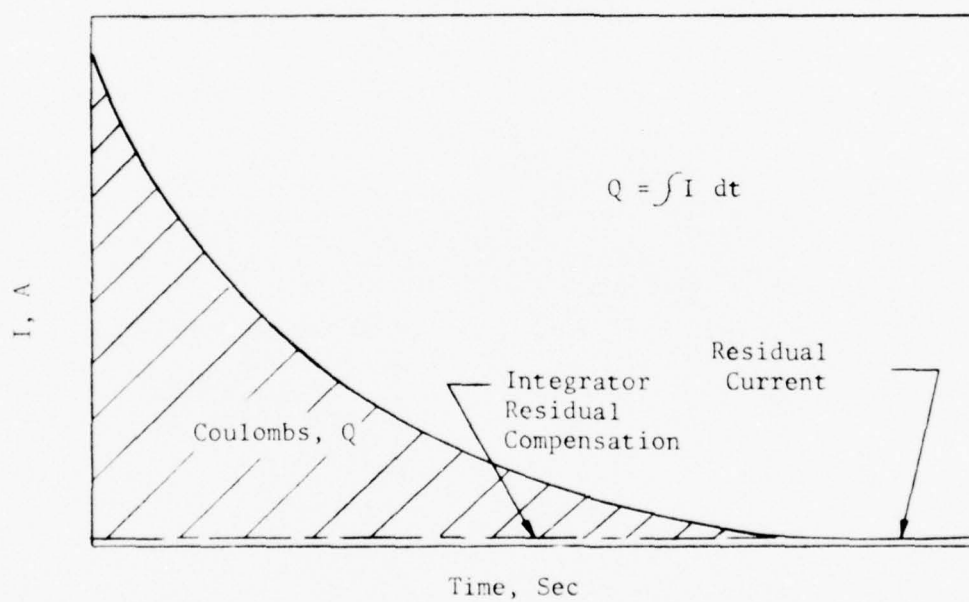


FIGURE 23 ILLUSTRATION OF COULOMETRIC MEASUREMENT

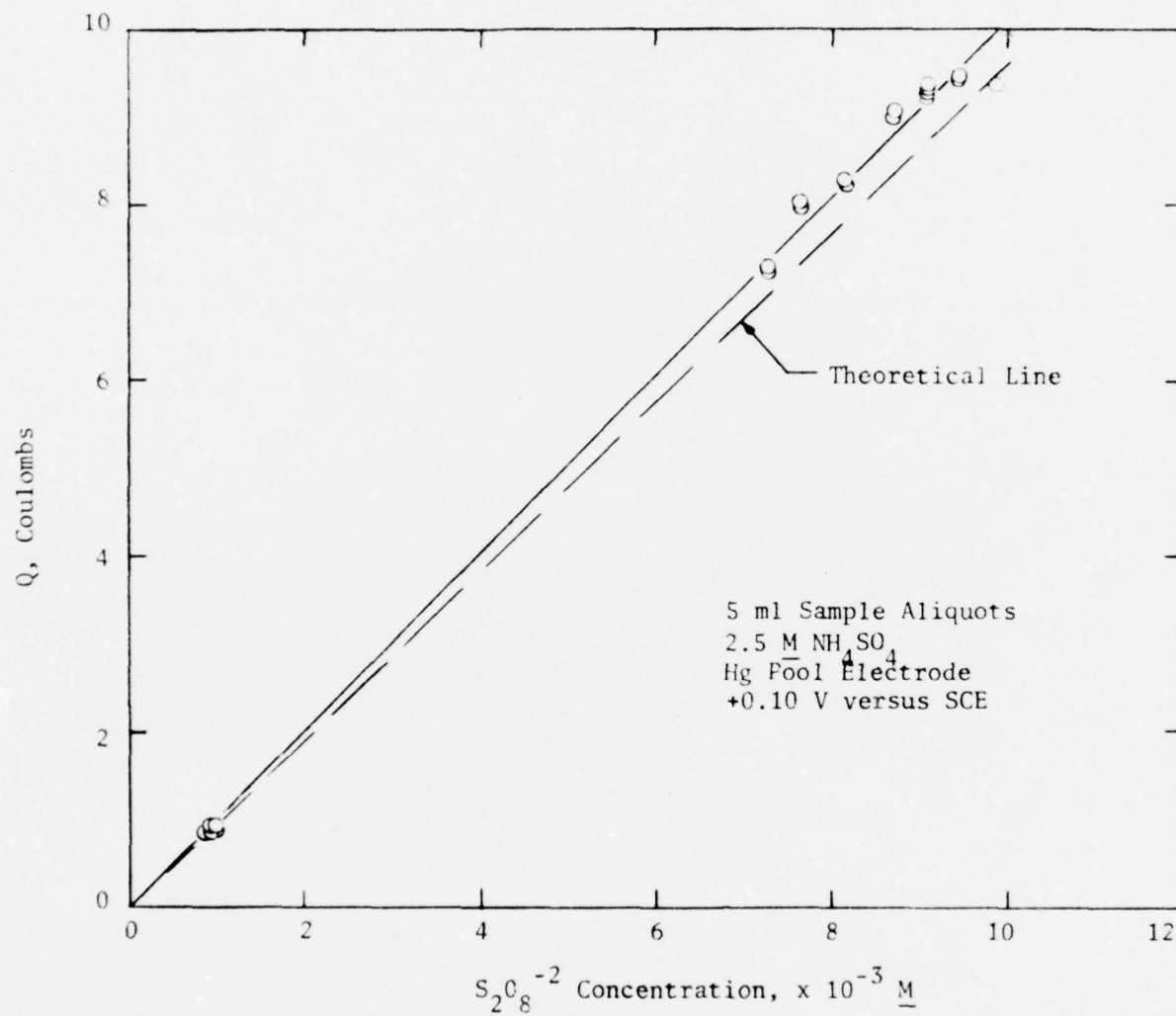


FIGURE 24 COULOMETRIC PERSULFATE SENSOR RESPONSE

calculated from Equation 14 is also shown. The data points in Figure 24 were collected over the entire test program, and the potential of the Hg pool electrode in all cases was +0.1 V versus SCE. The precision of the sensor is relatively good, but the actual response is somewhat greater than that theoretically calculated. Perhaps the spectrophotometric technique used to measure the persulfate concentrations results in a small negative error. In any case, the sensor produces a linear response curve over a wide range of persulfate concentrations.

The response of the sensor to COD can be simulated by introducing samples into the sensor which contains persulfate concentrations that would correspond to COD values if the sensor was part of the Electrochemical COD Analyzer. The simulated response to COD is displayed in Figure 25. Because this curve represents an expansion of the curve in Figure 24, the deviation between the experimentally determined curve and the theoretically predicted line is greater than in Figure 24. The curve has a negative slope because, as COD concentrations increase, the concentration of persulfate remaining after the organic oxidation decreases. Good precision is indicated at all COD concentrations studied, with only one group of data points off the curve.

Interference Study

The effects of several potential interferences on the performance of the coulometric persulfate sensor were investigated. The first potential interferences investigated were dissolved O_2 and O_3 .

Oxygen and O_3 Interference Tests. The response of the persulfate sensor to solutions containing O_2 and O_3 were of prime importance because of the demonstrated interference of dissolved O_2 with the amperometric persulfate sensor.

The coulometric persulfate sensor does not respond to O_2 or O_3 . Test No. 1 listed in Table 3 demonstrates that O_2 dissolved in an air-saturated sample of electrolyte is not reduced at the Hg pool electrode. Five milliliters of air-saturated electrolyte added to the cell produced no reduction current, and therefore no coulometric response.

In Tests No. 2 and No. 3, the response of the coulometric sensor to dissolved O_3 was investigated. Ozone is produced in the persulfate generation cell at high current densities. Therefore, O_3 may reach the coulometric sensor either from the persulfate generation cell or from the analysis of ozonated water.

Test No. 2 involved the analysis of a solution containing 9.45×10^{-3} M persulfate. This sample contained no dissolved O_3 . The coulombs resulting from the reduction of the persulfate were 9.420. When an identical persulfate sample was ozonated and the dissolved O_3 concentration was 2.2 ppm, the coulombs from that solution equalled 9.448. This demonstrates that O_3 produces no significant response in the coulometric sensor.

Inorganic Salts Study. The response of the persulfate sensor to solutions which contain inorganic ions was tested during this study. The results are

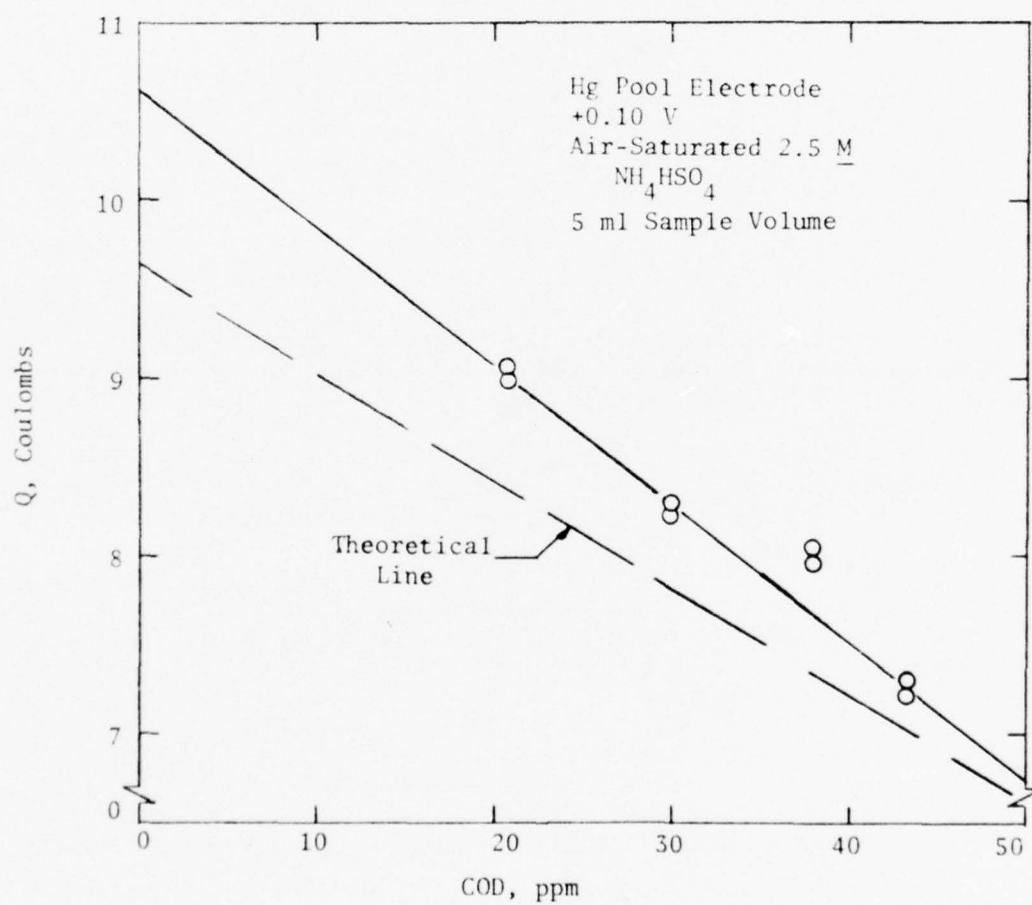


FIGURE 25 RESPONSE OF COULOMETRIC COD SENSOR

TABLE 3 RESULTS OF PERSULFATE SENSOR INTERFERENCE STUDY --
DISSOLVED O₂ AND O₃

	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
Sample Volume, ml	5.0	5.0	5.0
(NH ₄) ₂ S ₂ O ₈ Concentration, <u>M</u>	0	9.45 x 10 ⁻³	9.45 x 10 ⁻³
NH ₄ HSO ₄ Concentration, <u>M</u>	2.5	2.5	2.5
Dissolved O ₂ , ppm	8.0	N.D. (a)	N.D.
Dissolved O ₃ , ppm	0	0	2.2
Coulombs	0	9.420	9.448

(a) N.D. = Not Determined

shown in Table 4. As in the case of the persulfate generation cell, Test No. 3 simulates the condition of 30 days operation with water containing 150 ppm Cl^- , 10 ppm NO_3^-/N and 0.3 ppm Fe^{+2} . The accumulation of these species in the electrolyte recycle loop results in the concentration of the ions listed in Test No. 3. Test No. 2 represents the initial condition when this sample water is first analyzed and the concentrations of the three inorganic species have not increased in the recycle loop. Test No. 1 is a blank containing no interferences. In all three tests the concentration of the persulfate equalled $9.08 \times 10^{-3} \text{ M}$.

As the concentration of the inorganic salts increased during the test, the response of the sensor decreased from 9.350 to 9.235 coulombs. This is a relatively small decrease, which would result in an error of only 1.2%. Incorporation of the persulfate sensor in the Electrochemical COD Analyzer could be made such that automated calibration of the sensor would compensate for small changes in response such as this.

Persulfate Sensor Summary

The evaluation of sensors for monitoring persulfate in the Electrochemical COD Analyzer progressed from the simplest electroanalytical techniques to more sophisticated ones. However, the evaluation also progressed from sensors producing non-linear and error-prone response to a sensor that provides linear response to persulfate over a wide range of concentrations, good precision, and a high degree of freedom from interferences due to inorganic salts, dissolved O_2 , and O_3 .

The coulometric sensor meets the requirements of the Electrochemical COD Analyzer, but it will require a small modification of the original analyzer conceptual design since it is a batch-type device instead of a continuous, flow-through sensor. Also, for field applications, the coulometric sensor must be designed to avoid discharge of Hg from the pool electrode. Further development may later result in other more suitable electrode materials for field applications, but if such electrode materials are unavailable, appropriate cell designs are possible that will prevent discharge of Hg.

The analytical specifications of the coulometric persulfate sensor are summarized in Table 7.

pCO_2 SENSOR

The pCO_2 sensor is in the conceptual design of the Electrochemical TOC Analyzer to monitor the concentration of CO_2 produced by the oxidation of organic solutes. The concentration of this CO_2 is proportional to the TOC content in the sample. The small size, simple operation and relatively low cost of the membrane pCO_2 electrode are characteristics that resulted in its selection for use in the analyzer. Other CO_2 sensors, such as the infrared photometric types, are many times larger, more costly, and more complicated.

Operation of the pCO_2 Sensor

The pCO_2 sensor consists of a probe covered with a CO_2 permeable membrane. The sensor is schematically shown in Figure 26. During operation the acidic

TABLE 4 RESULTS OF PERSULFATE SENSOR
INORGANIC SALTS INTERFERENCE STUDY

	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
Sample Volume, ml	5.0	5.0	5.0
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ Concentration, <u>M</u>	9.08×10^{-3}	9.08×10^{-3}	9.08×10^{-3}
NH_4HSO_4 Concentration, <u>M</u>	2.5	2.5	2.5
NaCl Concentration, <u>M</u>	0	2.1×10^{-3}	3.6×10^{-2}
NaNO_3 Concentration, <u>M</u>	0	3.6×10^{-4}	6.1×10^{-3}
FeSO_4 Concentration, <u>M</u>	0	2.7×10^{-6}	0
$\text{FeNH}_4(\text{SO}_4)_2$ Concentration, <u>M</u>	0	0	4.7×10^{-5}
Coulombs #1	9.390	9.290	9.226
#2	9.310	9.274	9.243
Average	9.350	9.282	9.235

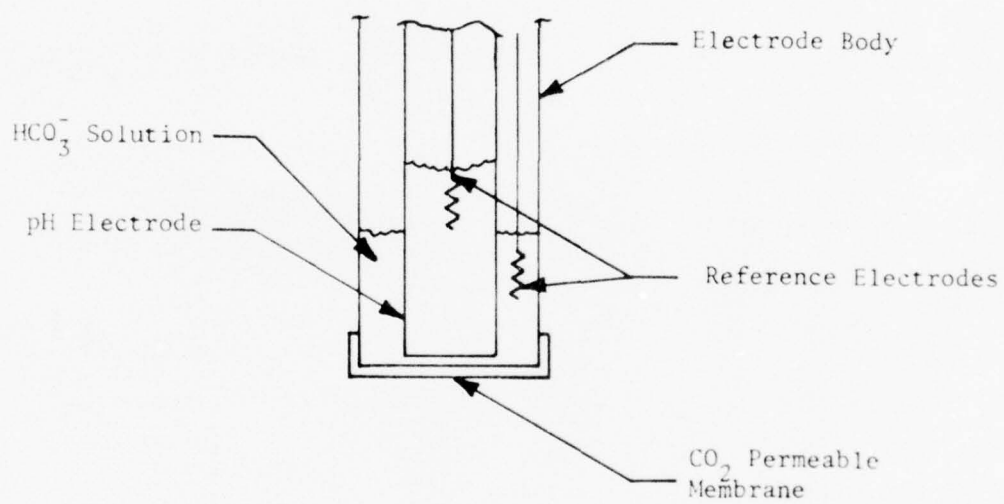
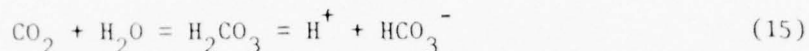


FIGURE 26 SCHEMATIC OF pCO₂ ELECTRODE

electrolyte from the Electrochemical TOC Analyzer flows beneath the membrane, and CO_2 from that solution diffuses through the permeable membrane into the internal filling solution of the sensor. The internal filling solution contains bicarbonate (HCO_3^-), and dissolution of CO_2 in the HCO_3^- solution increases its acidity by producing carbonic acid (H_2CO_3), which dissociates into H^+ and HCO_3^- .



The pH change in the internal filling solution is monitored by a glass pH electrode and reference electrode inside the sensor. The response of the pCO_2 electrode, E, is the voltage difference between these pH and reference electrodes. The sensor response is related to the logarithm of the CO_2 partial pressure in the test sample, as shown in Equation 16.

$$E = E' + 2.303 \frac{RT}{F} \log \text{pCO}_2 \quad (16)$$

where

$E' = \text{Constant, V}$
 $\text{pCO}_2 = \text{Partial pressure of } \text{CO}_2, \text{ atm.}$

pCO_2 Sensor Test Program

A commercial style of pCO_2 electrode was selected for use during this evaluation. The sensor was fitted with a flow-through cell for on-line measurements. The first activity of the sensor test program was the modification of the sensor to achieve balanced osmotic pressure on each side of the membrane. Because the CO_2 permeable membrane of the pCO_2 sensor is permeable to all vapors, the osmotic pressure of the electrolyte solutions on each side of the membrane must be equal. Otherwise, water vapor will transport from one side of the membrane to the other, and the concentration of the electrolyte within the sensor will change. The concentration change produces a drift in the sensor voltage and possibly an error in the TOC concentration measurement.

An internal filling solution was used with the sensor that had an osmotic pressure equal to that of 2.5 M NH_4HSO_4 , the electrolyte in contact with the sensor in the Electrochemical TOC Analyzer. This internal filling solution was developed during a previous Internal Research and Development (IRAD) program, which involved an earlier pCO_2 sensor in a similar electrolyte system.

After modification of the pCO_2 electrode, tests of the sensor were begun. The test program consisted of initial checkout of the sensor and studies of temperature, flow rate, electrolyte concentration, and interference effects. The test program concluded with measurement of the short-term precision and day-to-day reproducibility of the sensor response.

Checkout Tests

The response of the pCO_2 sensor to TOC concentrations was simulated by mixing samples containing sodium bicarbonate (NaHCO_3) with equal volumes of 5 M NH_4HSO_4 . Mixing the NaHCO_3 solutions with electrolyte in this way simulated mixing sample water containing organic solutes with the electrolyte in the

recycle loop of the Electrochemical TOC Analyzer, and then oxidizing those solutes with persulfate. All concentrations reported in this section therefore correspond to the simulated TOC concentrations of water samples as they would be measured by the Electrochemical TOC Analyzer. The water used to prepare these simulated TOC samples was boiled and sparged with nitrogen (N_2) to remove inorganic carbon prior to preparation of the $NaHCO_3$ solutions.

The response of the pCO_2 sensor to TOC is shown in Figure 27. Data points collected during two separate tests are shown. The response curve is linear from 0.5 to more than 500 ppm TOC. The detection limit is approximately 0.1 ppm TOC, and the response curve shows good day-to-day repeatability.

Temperature Study

Equation 16, which relates the theoretical response of the sensor to CO_2 concentrations, contains a temperature coefficient. Normally, the pCO_2 sensor was operated at ambient temperatures during this test program. However, during the temperature study, the temperature of the solution entering the pCO_2 sensor was varied and measured while the sensor response was monitored.

The theoretically predicted temperature coefficient for the sensor can be calculated from Equation 16, and is 0.2 mV/C when the concentration of TOC equals 10 ppm. The actual temperature coefficient of the pCO_2 sensor was determined for several TOC concentrations, and the measured coefficients ranged from 0.2 to 0.6 mV/C (Figure 28). The average coefficient was 0.5 mV/C.

Because of the logarithmic nature of the sensor response, the temperature coefficient can result in significant errors when the concentration of TOC is greater than 10 ppm. For example, when the TOC concentration is 5 ppm, a 1C temperature change will result in an error of less than 0.1 ppm TOC. However, when the concentration is 50 ppm, a 1C temperature change results in an error of about 0.7 ppm TOC. It is therefore probable that integration of pCO_2 sensor in the Electrochemical TOC Analyzer will include a temperature control device for maintaining the sensor temperature at a controlled, baseline value.

Flow Rate Study

The pCO_2 sensor is not sensitive to variations in the flow rate of the test solution. This was verified using flow rates ranging from 0.1 to 10.0 ml/min. Test solutions containing 0 ppm and 5 ppm TOC were used during the test, and the response of the sensor at all flow rate values was the same as that obtained at the baseline flow rate of 2.0 ml/min. It is therefore concluded that small fluctuations in the flow rate of electrolyte in the Electrochemical TOC Analyzer will not result in errors in TOC measurement.

Electrolyte Concentration Study

Because of the effect of osmotic pressure differences across the membrane in the pCO_2 sensor, the concentration of the electrolyte in the recycle loop of the Electrochemical TOC Analyzer will have an effect upon the response of the sensor. This effect was quantified during the electrolyte concentration

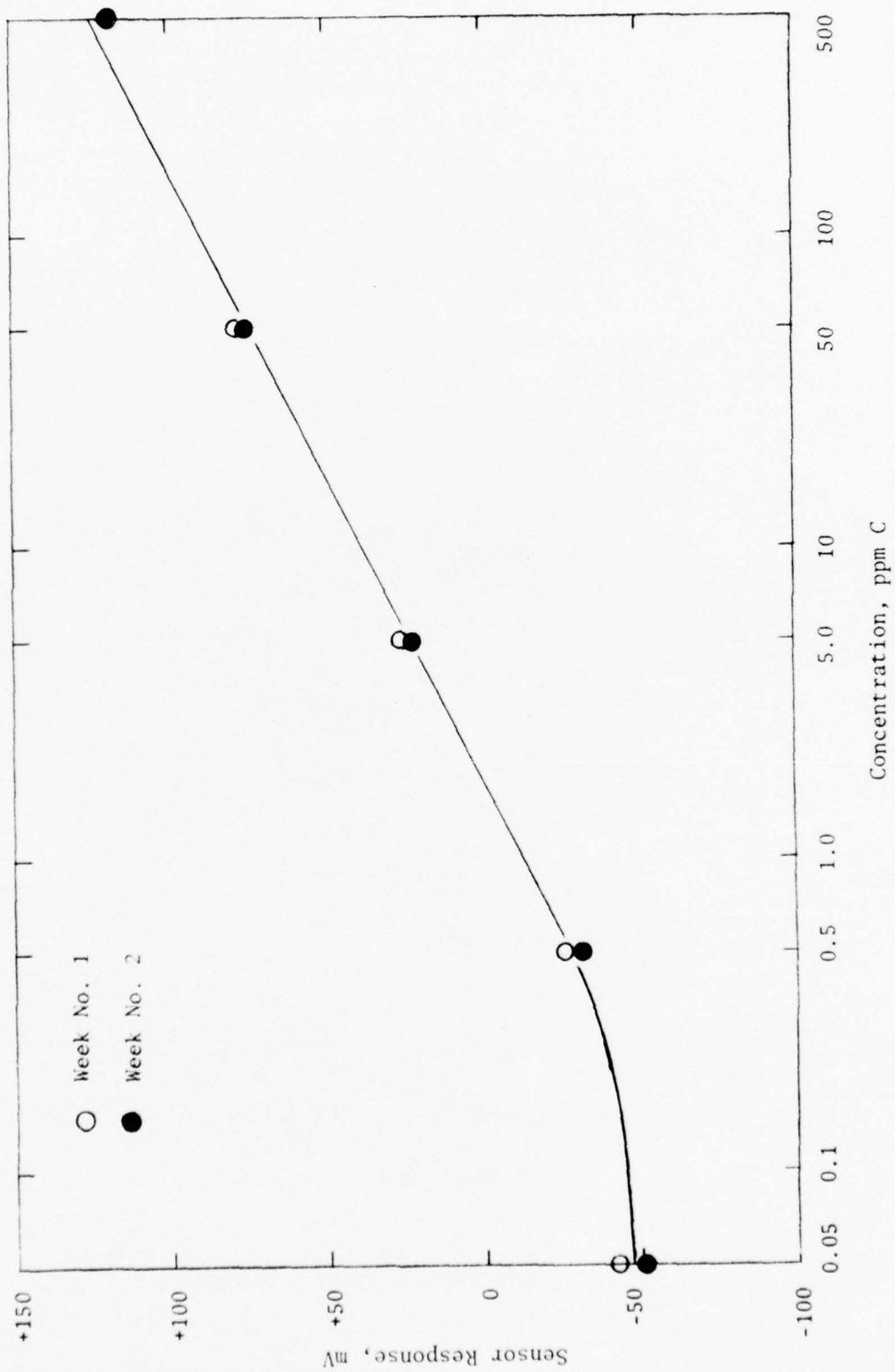


FIGURE 27 pCO₂ SENSOR RESPONSE CURVE

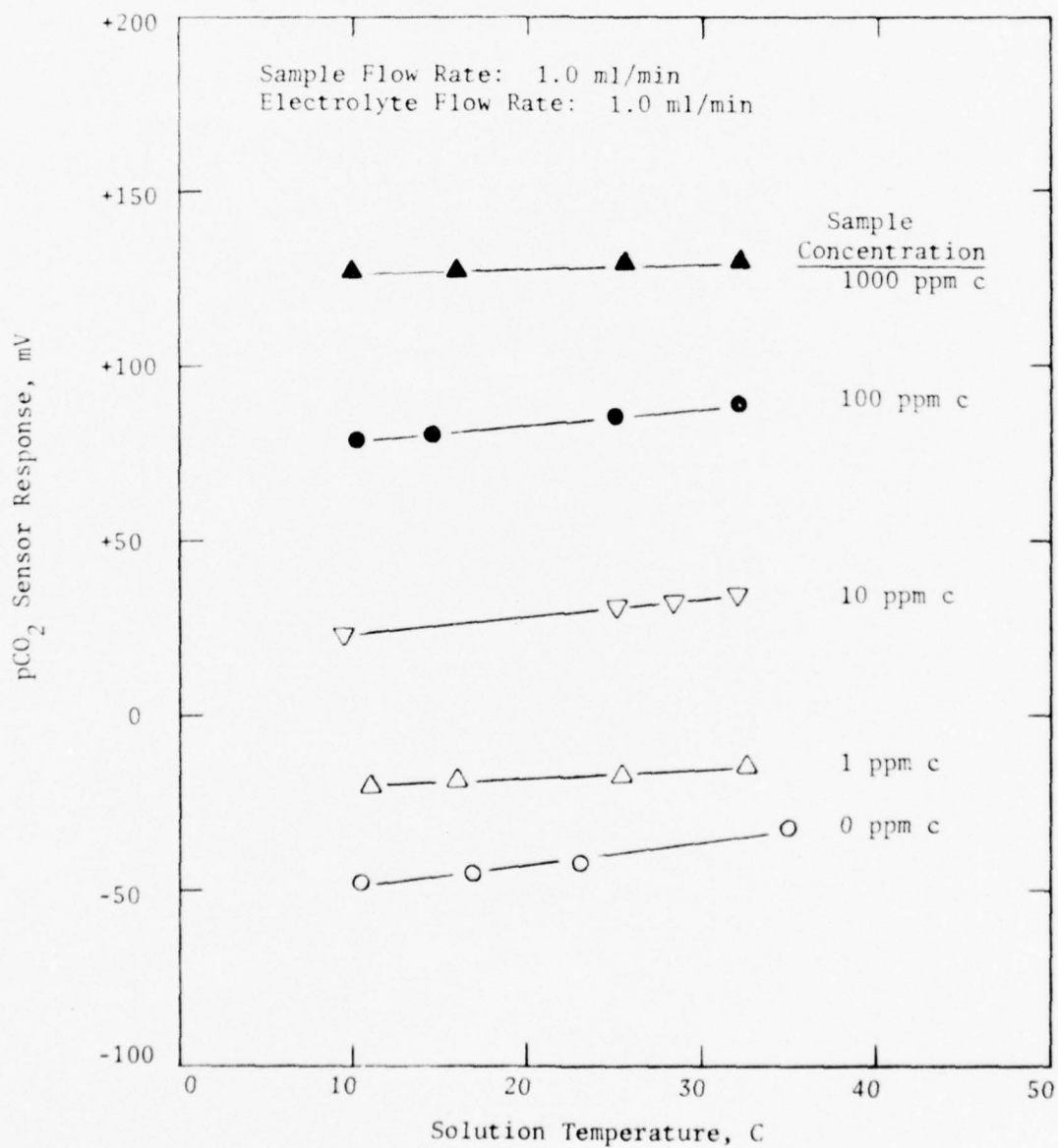


FIGURE 28 SOLUTION TEMPERATURE EFFECTS

study. As shown in Figure 29, an increase in the concentration of the electrolyte in the analyzer will produce a small increase in the output of the sensor. However, the difference between the curves for 0 and 5 ppm TOC remains constant, indicating that the sensitivity of the sensor remains unchanged. Therefore, in the Electrochemical TOC Analyzer, automated calibration of the pCO_2 sensor or control of the concentration of electrolyte in the recycle loop will compensate or avoid sensor output variations due to changes in the electrolyte concentration.

Interference Study

An advantage of the pCO_2 sensor is that the membrane separating the external test solution from the internal electrolyte tends to prevent interferences from many species. Only volatile species which are capable of diffusing through the membrane and changing the pH of the internal solution, or which prevent normal diffusion of CO_2 through the membrane, produce significant interferences. Relatively few species are capable of interfering in these ways.

With respect to the analyzer application, two general types of interferences were considered during this testing program. These interferences are inorganic salts and organic solutes. Inorganic salts were considered since they will be introduced into the analyzer's electrolyte recycle loop, and will tend to be concentrated as electrolyte is recycled. Organic solutes were considered since under some conditions oxidation of organic solutes may be incomplete. Therefore, low concentrations of organic solutes may sometimes exist in the electrolyte, and the possible effects of these residual organics were investigated.

Inorganic Salts Study. Table 5 summarizes the response of the pCO_2 sensor to solutions containing Cl^- , NO_3^- , and Fe^{3+} ions. Test No. 3, as in the case of the other salt interference studies performed during this program, represented a situation in which salts were concentrated in the electrolyte recycle loop over a 30-day period. Test No. 2 involved salt concentrations one half those used in Test No. 3. Test No. 1 was a blank containing no inorganic interferences.

The response of the sensor to samples containing 5 ppm TOC plus the concentrations of salts shown in Table 5, decreases from 12 to 4 mV as the concentration of the salt mixture increases.

The sensor response to the inorganic solutes is probably the result of small changes in the osmotic pressure on the sample side of the sensor membrane. None of the ionic solutes are capable of diffusing readily through the membrane or changing the pH of the internal filling solution. The buildup of inorganic species in the electrolyte recycle loop will be a slow process, resulting in a slow drift of the sensor output. It is therefore anticipated that relatively infrequent recalibration of the pCO_2 sensor will adequately compensate for the sensor response to the salts. Since automated calibration of the pCO_2 sensor is a highly desirable feature of the Electrochemical TOC Analyzer anyway, the presence of inorganic solutes in the electrolyte recycle loop presents no significant difficulty.

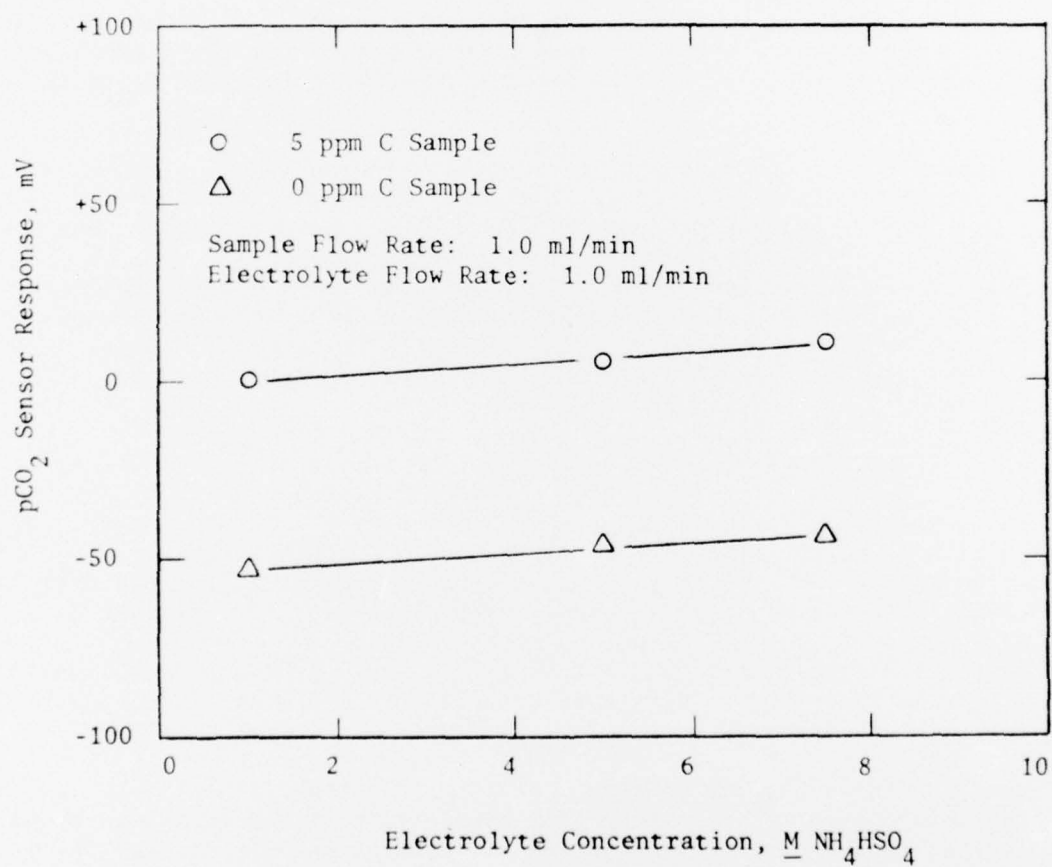


FIGURE 29 ELECTROLYTE CONCENTRATION EFFECTS

TABLE 5 EFFECTS OF INORGANIC SALTS ON pCO_2
SENSOR PERFORMANCE

	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
Electrolyte Concentration, $\text{M NH}_4\text{HSO}_4$	5.0	5.0	5.0
Electrolyte Flow Rate, ml/min	1.0	1.0	1.0
Sample Concentration:			
Carbon, ppm	5.0	5.0	5.0
NaCl, M	0	3.6×10^{-2}	7.2×10^{-2}
NaNO_3 , M	0	6.1×10^{-3}	1.2×10^{-2}
$\text{FeNH}_4(\text{SO}_4)_2$, M	0	4.7×10^{-5}	9.4×10^{-5}
Sample Flow Rate, ml/min	1.0	1.0	1.0
Sensor Response, mV			
Run No. 1	+11	+6	+3
Run No. 2	+12	+10	+5
Average	+12	+8	+4

Organic Solute Study. The results of the organic solute interference study are listed in Table 6. Test No. 1 was performed as a blank and that test solution contained no organic solutes. Tests No. 2 and No. 3 involved solutions which contained urea, methanol, ethanol, phenol and acetic acid at concentrations of 1 ppm and 5 ppm TOC, respectively.

As the organic solute concentration in the test solution increases, the sensor response decreases only from +17 mV to +12 mV. This response change may be due to osmotic pressure changes or the influence of the organic solutes upon the transport of CO_2 through the membrane. In any case, the change is less significant than that observed in the case of inorganic salts.

Like inorganic salts, any buildup of organic solutes in the electrolyte recycle loop will be slow, and will result in a drift in sensor response. Normally, such a buildup will not occur because of the quantitative efficiency of the organic oxidation. In any case, automated calibration of the pCO_2 sensor, as discussed above, will eliminate errors due to sensor drift from organic solutes.

Reproducibility Tests

Good short-term precision and day-to-day reproducibility were demonstrated by the sensor. The short-term precision of the sensor was quantified by recording its response to a solution containing 5 ppm TOC over a 7-hour period. This data is shown in Figure 30. Generally, the sensor response varied no more than 1 mV from the average value of +17 mV. The average response was constant, even though the temperature of the sensor followed ambient conditions.

The day-to-day reproducibility of the sensor response was quantified and is shown in Figure 31. The response of the sensor was measured for samples containing 0 ppm and 5 ppm TOC. On most occasions, the difference between the response to the two solutions was approximately constant. However, the day-to-day fluctuations of the response were greater than those measured during the short-term test. This is probably due to significant daily variations in the ambient temperature.

The precision and reproducibility tests have demonstrated that the pCO_2 sensor performs well over moderately long periods of time and results in precise data during shorter periods. Temperature control of the pCO_2 sensor is required for better day-to-day reproducibility, and may increase short-term precision.

pCO_2 Sensor Summary

The pCO_2 sensor has demonstrated the required sensitivity and detection limit for use in the Electrochemical TOC Analyzer. The sensor is relatively free of inorganic and organic interferences. It is insensitive to flow rate variations, but the concentration of the electrolyte in the analyzer recycle loop and the temperature of the sensor are parameters that must be controlled.

The results of the reproducibility tests and the other tests performed on the pCO_2 sensor have demonstrated the need for automated calibration. With a

TABLE 6 EFFECT OF ORGANIC SOLUTES ON pCO_2 SENSOR

	<u>Test No. 1</u>	<u>Test No. 2</u>	<u>Test No. 3</u>
NH_4HSO_4 Concentration, <u>M</u>	5.0	5.0	5.0
Total Flow Rate, ml/min	2.0	2.0	2.0
Sample Concentration, ppm C	5.0	5.0	5.0
Urea Concentration, ppm TOC	0	1.0	5.0
Methanol Concentration, ppm TOC	0	1.0	5.0
Ethanol Concentration, ppm TOC	0	1.0	5.0
Phenol Concentration, ppm TOC	0	1.0	5.0
Acetic Acid Concentration, ppm TOC	0	1.0	5.0
Sensor Response, mV			
Run No. 1	+17	+16	+12
Run No. 2	+16	+15	+11
Run No. 3	+17	-	-
Average	+17	+16	+12

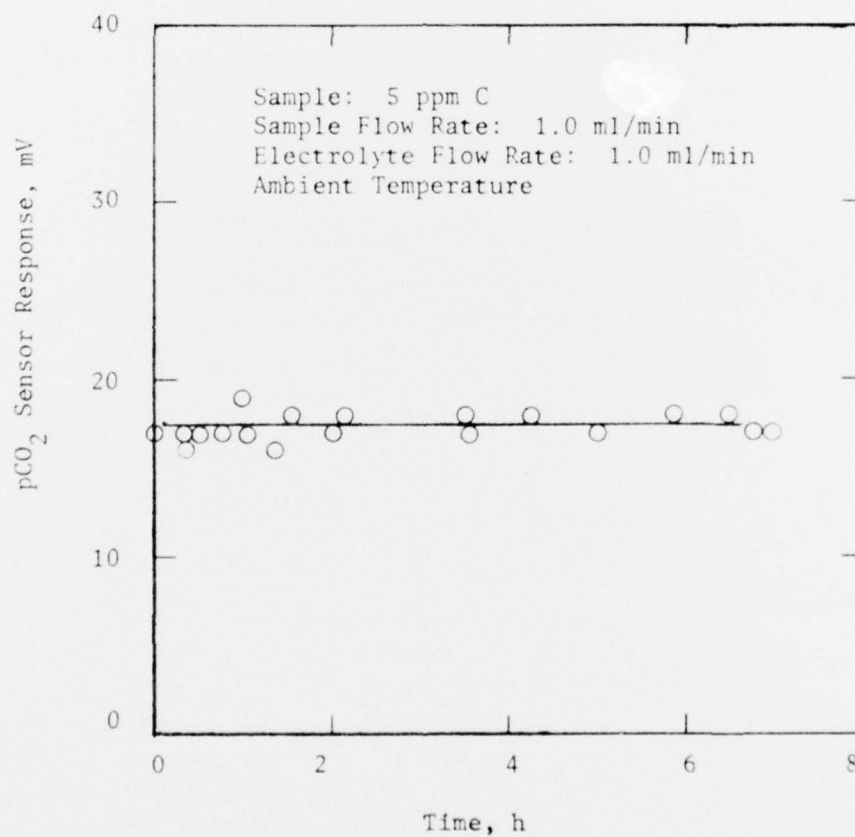


FIGURE 30 PRECISION OF pCO₂ SENSOR

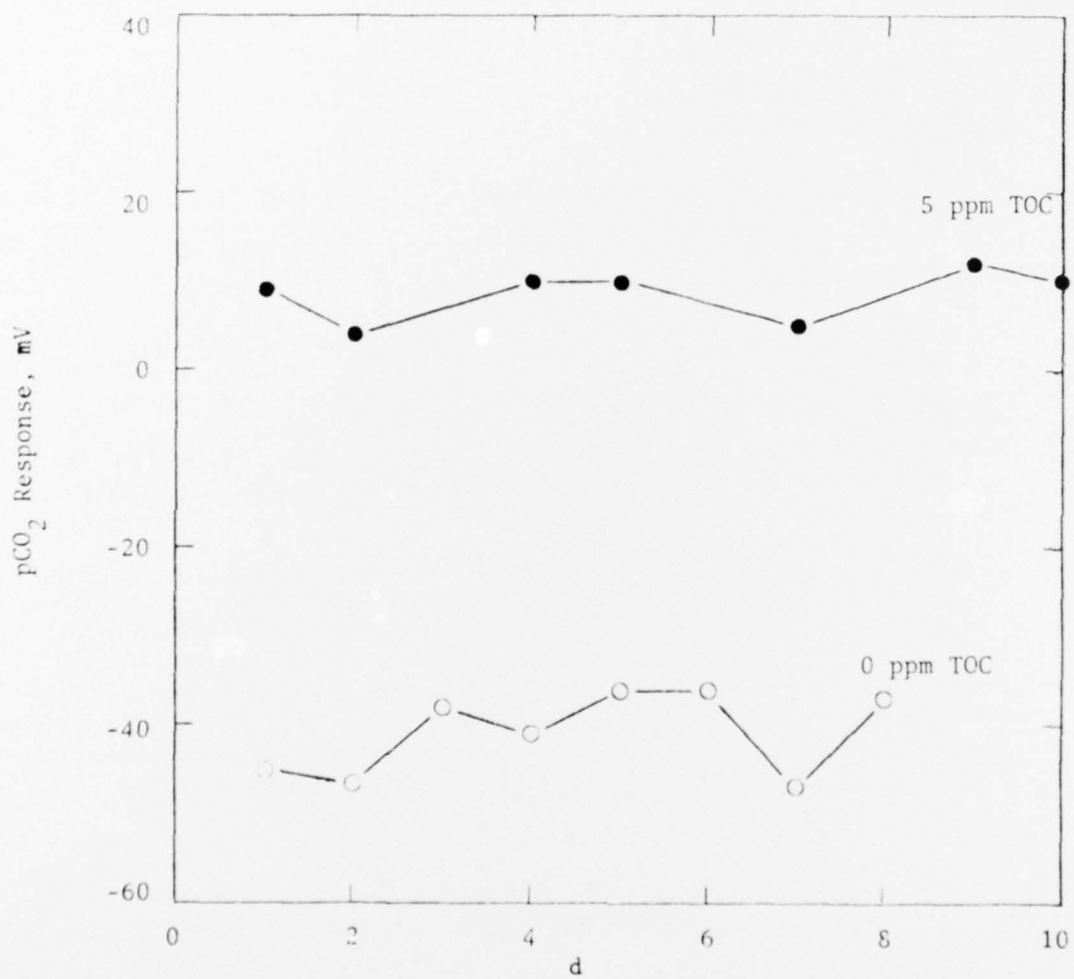


FIGURE 31 DAY-TO-DAY REPRODUCIBILITY STUDY OF pCO₂ SENSOR

simple calibration technique, the response of the sensor may be compensated for variations in the electrolyte concentration and concentration of organic and inorganic solutes in the electrolyte recycle loop. The effect of temperature on the pCO_2 sensor can be eliminated by controlling the sensor temperature or compensating its output using the theoretically predicted temperature coefficient from Equation 16. It is anticipated that the pCO_2 sensor will provide accurate and reliable TOC concentration data if these considerations are addressed during integration of the sensor into the Electrochemical TOC Analyzer.

The analytical performance of the pCO_2 sensor and other components evaluated during this program are summarized in the next section.

COMPONENT PERFORMANCE SUMMARY

The analytical performance and certain hardware considerations of the persulfate generation cell and sensors are summarized in Table 7.

Besides the operating range of the components, discussed in preceding sections, the table lists the readout frequency of the sensors. The pCO_2 sensor provides continuous readout, while the persulfate sensor produces a new concentration value every 20 minutes. This time period is dependent upon the cell design, stirring rate and ratio of sample volume to electrode area. By using smaller samples and an improved sensor design, the frequency could be increased to three minutes per update.

The pCO_2 sensor produced the least precise and reproducible data. This is probably due to the lack of temperature control or compensation. With either of these features, the repeatability of the pCO_2 sensor can be improved.

The size and weight of the components are small with respect to the total dimensions of other TOC and COD analyzers. The largest of the three components is the persulfate sensor. It has a volume of 25 in³ and weighs slightly more than half a pound.

Only the persulfate generation cell consumes power, and it uses only 0.6 W at the baseline current of 100 mA. Clearly, none of these components will limit the portability of the Electrochemical COD and TOC Analyzers. Probably the electrolyte and sample pumps will be the largest analyzer components and will consume the most power.

During the test program, the persulfate generation cell and pCO_2 sensor required little operator labor each day, and none of the three components failed during the tests. The Mean-Time-Between-Failures (MTBF) listed in Table 7 are therefore estimates. The persulfate sensor required manual addition of the test solutions prior to each measurement. This resulted in the large amount of operator labor required for a continuous day of operation (72 min/day). Automated sampling, which would be part of integrating the persulfate sensor in the Electrochemical COD Analyzer, would greatly reduce this figure.

Future efforts will be required to develop durable versions of the components which are compatible with transportation and use in the field. Glass parts of the present laboratory versions of the components will be largely replaced by

TABLE 7 COMPONENTS PERFORMANCE SUMMARY

Parameter	$\text{S}_2\text{O}_8^{-2}$ Generation Cell	$\text{S}_2\text{O}_8^{-2}$ Sensor	pCO_2 Sensor
Capacity, $\text{M S}_2\text{O}_8^{-2}$	0.043 ^(a)	-	-
Detection Limit	-	0.5 to 1.0 ppm COD	0.1 ppm TOC
Upper Response Limit	-	140 ppm COD	500 ppm TOC
Readout Frequency, min/update	-	20	continuous
Short-term Precision, % average deviation	1.2	2.6 ^(b)	4.2 ^(c)
Daily Repeatability, % average deviation	4.4	2.2 ^(b)	9.9 ^(c)
Temperature Coefficient	$2.4 \times 10^{-4} \text{ M S}_2\text{O}_8^{-2}/\text{C}$	0	0.1 ppm TOC/C ^(c)
Weight, lb	0.05	0.55	0.2
Volume, in ³	2.4	25.1	3.6
Power, W	0.6 ^(d)	-	-
Operator Labor, min/day	4-5	72	15
Reliability (MTBF), hr	720	1000	720
Hardware Maturity	Laboratory Breadboard	Laboratory Breadboard	Advanced Breadboard
Calibration	None	Manual	Manual

(a) at 1.0 ml/min

(b) at 10 ppm COD

(c) at 5 ppm TOC

(d) at 100 mA

more rugged materials. Also, the manual calibration techniques used with the pCO_2 and persulfate sensors will be automated.

CONCLUSIONS

The objective of this program has been successfully achieved. The three essential components of the Electrochemical COD and TOC Analyzers have been tested and evaluated, and their performance meets or surpasses the design goals for use in the analyzers.

The breadboard persulfate generation cell successfully demonstrated the concept of in situ electrochemical generation of persulfate. With in situ generation of this reagent, analyzers which consume no reagents or compressed gases can be developed for field applications.

The persulfate generation cell is capable of generating 0.04 M persulfate in 5.0 M NH_4HSO_4 with a flow rate of 1.0 ml/min. This is about twice the concentration of persulfate projected for use in the analyzers. Other concentrations can be generated at various flow rates by proper sizing of the anode in the cell and use of appropriate currents.

The coulometric persulfate sensor was developed after tests of the potentiometric sensor, initially selected as the baseline persulfate sensor during the previous conceptual design effort, showed that potentiometric methods would not result in accurate, reproducible COD measurements.

Coulometric monitoring of persulfate will allow COD measurements over the range from about 0.5 ppm to at least 140 ppm COD. Dissolved O_2 and O_3 do not interfere as they do with other electrochemical techniques. Direct spectrophotometric techniques were shown to lack sensitivity and are subject to interferences. Other techniques are possible, but they consume reagents, and were not tested during this effort because of the development goal of analyzers which require no consumables.

The possible disadvantage of the coulometric persulfate sensor for some applications is the Hg pool electrode used to reduce persulfate in the sensor. However, operation of the sensor in the electrolyte recycle loop of the Electrochemical COD Analyzer is not anticipated to result in the discharge of Hg or mercury ions. Mercury ions will be reduced at the electrode when it is operating, and proper design of the sensor will result in no loss of Hg from the sensor even during transport of the analyzer.

The coulometric sensor using the Hg pool electrode is the first workable solution to the problem of persulfate monitoring without consumption of reagents. Use of the Hg electrode will allow COD measurements and further development of the COD Analyzer. Later, other electrode materials may be found to eliminate the use of Hg for those applications in which it is undesirable.

Total organic carbon measurements do not require the persulfate sensor. Instead, the pCO_2 membrane electrode is used to measure TOC values. It is capable of measurements over the range of 0.1 to more than 500 ppm TOC. The pCO_2 sensor used during this evaluation was a flow-through sensor that permitted continuous concentration readout.

The effects on the components due to salts accumulated in the electrolyte recycle loop of the analyzers were investigated. Tests were conducted in which solutions were prepared to simulate the composition of the electrolyte after 30 days of continuous analysis of a solution containing 150 ppm Cl^- , 10 ppm NO_3^-/N , and 0.3 ppm Fe^{+2} . These solutions improved the performance of the persulfate generation cell and had relatively little effect on the sensors. Therefore, at least in the case of common inorganic salts, the buildup of contaminants within the electrolyte recycle loop is anticipated to result in few if any problems.

The components test program has demonstrated the need for certain features in the end-item analyzers. For example, means for adjusting the cell current in the persulfate generation cell should be provided in order to generate a constant concentration of persulfate. This adjustment will compensate for temperature and electrolyte concentration variations, plus the presence of inorganic salts in the electrolyte. The coulometric persulfate sensor is a batch-type sensor, and the interface between the electrolyte recycle loop and sensor must provide for batch operation. The pCO_2 sensor should be temperature controlled or compensated for temperature variations. Finally, the end-item analyzers should have provisions for automated calibration to result in the most accurate and reproducible TOC and COD measurements.

The special requirements of the components are not mutually exclusive. Therefore, the possibility exists for developing an analyzer that measures both TOC and COD concentrations by combining the persulfate generation cell and both sensors in a single analyzer. This analyzer, the Electrochemical TOC/COD Analyzer, was discussed during the previous feasibility analysis of the individual Electrochemical COD and TOC Analyzers. The evaluations of the components performed during this program support the possibility of integrating all three components.

Although individual components have been evaluated, the actual performance of the Electrochemical TOC, COD or TOC/COD Analyzer must yet be demonstrated. This is because the analytical performance of the analyzer depends not only on the performance of the sensors and persulfate generation cell, but also upon the efficiency of the organic oxidation process occurring within the analyzer. Incomplete oxidation of the organic solutes, or oxidation of inorganic species in the sample, may produce significant errors in one or both of the TOC and COD measurements.

Because of these considerations, the effectiveness of the organic oxidation process and its effect upon the analytical performance of the analyzers should be investigated prior to future hardware development and component integration activities.

RECOMMENDATIONS

The tests so far conducted have shown that the persulfate generation cell and persulfate and pCO_2 sensors meet the performance requirements of the Electrochemical COD and TOC Analyzers. Combining both sensors in a single analyzer for simultaneous measurement of TOC and COD concentrations appears to be feasible. These measurements are based on the oxidation of organic solutes

and measurement of the CO_2 produced during the oxidation, or the quantity of persulfate consumed during the oxidation. It has been concluded that prior to future hardware development the quantitative efficiency of the organic oxidation process should be investigated and the effects of possible interferences studied.

The oxidation of organic solutes by persulfate is a kinetically slow process. Catalysts are normally used to increase the rate of the oxidation to useful levels. Ultraviolet radiation can be used as a catalyst, and it provides a convenient method of catalyzing the reaction because no chemicals need to be added. Life Systems previously developed UV reactors for use in a Continuous, Chemical TOC Analyzer. The analyzer was developed under an IRAD program and was based on the persulfate oxidation technique. The analyzer contained two UV reactors, and these reactors are now available.

It is recommended that one or both of Life Systems' UV reactors be integrated with the pCO_2 and persulfate sensors tested during the present effort. The reactor and sensors will be used to investigate the analytical performance that may be obtained from a future prototype or end-item TOC/COD Analyzer. The UV reactor and sensors, plus a pump, fittings and other hardware required to integrate them, will constitute the Breadboard Electrochemical TOC/COD Analyzer. Samples will be manually prepared and persulfate will be added to simulate the function of the persulfate generation cell. Since most samples are synthetic, manual addition of persulfate will only slightly increase operator labor. This is recommended because development and integration of the persulfate generation cell and other pieces of hardware required for a completely automated analyzer can be postponed until the results of the analytical evaluation of the Breadboard Analyzer are obtained.

Recommended tests of the Breadboard Analyzer include an initial checkout, parametric tests, interference studies, and tests of the analyzer's response to synthetic and real samples.

The parametric tests will be designed to indicate the concentration of persulfate and the UV reactor residence time that are optimum for measurement of TOC and COD values. The sensors will be used to judge the efficiency of the organic oxidation process under each set of conditions tested.

Inorganic salts and particulate matter are possible interferences which will be investigated. It is suggested that Cl^- , NO_3^- and Fe^{+3} be included among the inorganic interferences. Candidate inorganic particulate materials are silica and Arizona road dust.

Following identification of the optimum experimental parameters for the breadboard Electrochemical TOC/COD Analyzer, the performance of the analyzer will be quantified with a variety of simulated and real samples. This test will serve to check the efficiency of the oxidation process for a variety of organic solutes. It is recommended that during the first part of this test, solutions containing individual organic solutes be used. These solutes will be selected because of their frequent presence in water samples, or because they represent a group of organic solutes that are frequently present. The second part of the test will consider real samples and a comparison of the results obtained with the Breadboard Analyzer to results obtained with standard methods.

It is recommended that techniques that may be utilized with the Electrochemical TOC/COD Analyzer to permit measurement of particulate organic carbon concentrations be surveyed and evaluated. This effort would possibly consider techniques to disrupt particulates prior to analysis, such as thermal digestion and destruction by ultrasonic or mechanical means.

Following testing and evaluation of the Breadboard Electrochemical TOC/COD Analyzer, it is recommended that the development of a prototype version be performed. Automated sampling and inorganic carbon removal techniques should be part of the prototype analyzer, and the persulfate generation cell will be included for in situ generation of the reagent. Other modification to the analyzer design, shown to be required by the tests of the breadboard analyzer, will be incorporated into the prototype design. The prototype analyzer also will be designed to achieve required levels of durability and reliability. A feedback control function may be incorporated into the prototype design for control of water treatment processes. The prototype analyzer will then be tested to insure that it provides the performance, automation and reliability required for use in selected applications.

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